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THE FREE ENERGIES OF HYDRATION OF SOME ORGANIC COMPOUNDS.

By

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C O N T E N T S

C H A P T E R I.

Introduction.

Introduction.

The study of the properties of solutions has been one of the most important branches of physical chemistry since the seventeenth century. In spite of the enormous volume of work that has been done in this field, it is a fact that in only a very few simple cases can the experimental properties of the solutions be predicted from the theoretical considerations. In this thesis a study is made of binary solutions of which one of the components is water. Before the properties of mixtures are considered, it is necessary first to discuss the characteristics of pure liquids.

Liquids have been classified:- (1) normal, which have low dielectric constants and conform to the number of rules concerning surface tensions, heats of vaporisation, etc., (2) abnormal, which have again abnormally high dielectric constants, surface tensions and heats of vaporisation than would be expected on

the basis of normal liquids. This has been explained by the fact that the molecules in liquids are non-polar and polar, i.e., the latter possess permanent electric dipoles while in the former the centres of the positive and negative charges coincide. Attempts have therefore been made from time to time to distinguish between these types of liquids.

Trouton (Phil. Mag., 5 18, 54, 1884) put forward a rule, known as Trouton's rule, which states that the molar heat of vaporisation, L, divided by the boiling point in degrees Kelvin Tb, is a constant. This quotient is the entropy of vaporisation. For associated or polar liquids the extra energy absorbed in separating the polar molecules causes an abnormally large heat of vaporisation, and therefore the Troutons quotient is larger than the normal value. Empirical expressions have been proposed giving the Trouton's quotient in terms of boiling point by Bingham (J. Amer. C. S., 28, 723, 1906) and Forcand (Compt. rend., 28, 1439, 1648, 1809, 1913). Hildebrand (J. Amer. C. S., 37, 970, 1915 and 40, 45, 1918) gave a modified expression for Trouton's rule, which is known as Hildebrand's rule, according to which the entropy of vaporisation is the same for all normal liquids, not when the liquids are boiled under a constant pressure, but rather when the temperature and the pressure are

so chosen as to give the same concentration or volume of vapour in every case. In other words,

$$\frac{L}{T_c} = \text{constant},$$

where L = molar heat of vaporisation,

T_c = temperature for the given concentration.

Recently Langmuir (J. Amer. C. S., 54, 2798, 1932) has given an equation for the vapour pressures of liquids,

$$p = AT^{\gamma} \, Exp^{-b/T}$$

where p = vapour pressure of liquid,

T = absolute temperature,

and A, γ and b are constants.

He shows that Trouton's rule is equivalent to postulating that $\gamma = 0$ and A = a universal constant, whereas Hildebrand's rule is equivalent to taking $\gamma = 1$ and log A = 7.8; and suggests that when the value of γ is taken as 1.5, log A = 6.37, which gives a closer general agreement with the data.

Having discussed the nature of pure liquids, we may now turn to the consideration of binary liquid mixtures. Earlier work on this subject was done by Henry, Van't Hoff and Raoult.

Henry (Phil. Trans., 29, 1803; Gilb. Ann., 20, 147, 1805) studied the solubility of gases in liquids and found that the concentration in the liquids was proportional to pressure of the gases. This may be

expressed as

$$\frac{p_{(gas)}}{c_{(gas)}} = \text{Constant.}$$

In dilute solutions the various ways (molar fraction, weight and volume concentrations) of expressing the concentrations are nearly proportional to each other. If we use the molar fraction, we may write Henry's Law as

$$\frac{p_2}{N_2} = K_2 \qquad (1)$$

where p_2 = partial pressure of the gas,

N_2 = its molar fraction in liquid,

K_2 = Henry's Law Constant.

Raoult (Compt. rend., 104, 1430, 1887; Z. physik. Chem., 2, 353, 1888) found that the fractional lowering of the vapour pressure of a solvent by an involatile solute was equal to the molar fraction of the solute within a certain range of low concentrations. This may be expressed as

$$\frac{p^{o} - p_1}{p_1^{o}} = N_2$$

where p_1^{o} = vapour pressure of pure solvent,

p_1 = vapour pressure of the solution,

N_2 = molar fraction of the solute.

Alternatively, this may be written as

$$p_1/p_1^{o} = N_1, \text{ or } p_1 = p_1^{o}N_1 \qquad (2)$$

where N_1 = molar fraction of the solvent.

If it be applied also to the solute, we have

$$p_2 = p_2^{\circ} N_2 \qquad (3)$$

where p_2° = vapour pressure of a pure liquid.

It can be shown that Raoult's law is universally true for the solvent when the concentration of the solute is very small, provided that the molar fractions are properly evaluated; and it follows from thermodynamical principles that if Raoult's law is true under these conditions, Henry's law is also valid (Butler's Fundamentals of Chemical Thermodynamics, Volume II, page 83).* However Raoult's law does not necessarily hold over the whole range of solutions. G.N.Lewis (J.Amer.C.S., 30, 668,1908) discussing the validity of Raoult's law, proposed that solutions in which it holds over the whole range of

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* The fundamental equations for the partial free energies of the components of a very dilute solution are

(a) $\overline{F}_1 = \overline{F}_1^{\circ} - RT\, n_2/n_1$ per solvent

(b) $\overline{F}_2 = \overline{F}_2^{\circ} + RT \log n_2/n_1$ per solvent,

where n_2/n_1 = molar ratios of solute to solvent. Raoult's law follows from (a) and Henry's from (b); for if p is the partial pressure of the solute in the vapour,

$$\overline{F}_2 = \overline{F}_{g_2}^{\circ} + RT \log p$$

whence $p/(n_2/n_1)$ = Constant,
and if the solution is very dilute, n_2/n_1 can be identified with N_2.

composition from $N_2=1$ to $N_2=0$ should be regarded as ideal solutions. Then it is evident by comparison of (1) and (3) that the constant of Henry's law is $K_2=p_2^\circ$. This however is only true in a comparatively few cases. In the vast majority of systems deviations from Raoult's law occur, and the Henry's law constant (i.e. the ratio of pressure to molar fraction in a very dilute solution) does not coincide with the vapour pressure of the pure liquid. Thus for dilute solutions Henry's law is the general law, which is certainly true if the solution is sufficiently dilute. The identification of the Henry's law constant with p_2°, as is required by the extended application on Raoult's law, is a special case which is only valid for ideal solutions.

The deviations from Raoult's law which occur, when the molar fraction differs appreciably from unity, has been the subject of much investigation. Zawidski (Z. physik. Chem., 35, 129, 1900) in his partial vapour pressure measurements of binary solutions, found some cases in which Raoult's law was valid over the whole concentration range, but in most cases appreciable deviations occurred; and it would be impossible to describe in such a short space all the considerations that have been put forward to account for these deviations.

Generally speaking it may be said that the necessary conditions for the validity of Raoult's law is that the energy and nature of the interaction of the solute molecule with its surrounding molecules shall be the same in the solution as in the pure liquid solute. In general this can only be satisfied when a solvent molecule may be replaced by a solute molecule without any change of volume, and when the energy of interaction of solvent and solute molecules is the same as that between two solute molecules. Hildebrand (Solubility, pages 60-62) has stated as the conditions for the validity of Raoult's law that there shall be (1) no heat effect, (2) no volume change, when the pure liquids are mixed. While these conditions are no doubt necessary, they are probably not in all cases sufficient to ensure the validity of Raoult's law. Especially large heat effects and thus large deviations can be expected when solute and solution differ considerably in the polar character.

At one time the interactions between the solute and solvent molecules were classified as (1) chemical and (2) physical; and much discussion went on as to which of these groups were mainly responsible for deviations. Dolezalek and his co-workers (Z. physik. Chem., 64, 727, 1908, etc.) strongly supported the chemical view and accounted for all the deviations due

to chemical combination of some sort: e.g., compound formation or association of one or both components. With these effects it is possible to account for any deviation, but some of the assumptions made have been shown to be contrary to facts, and it has never been demonstrated unambiguously that the effects postulated actually occur.

On the other hand there are various physical interactions which appear to be capable of producing deviations. Van der Waals (Z. physik. Chem., 5, 133, 1890) attempted to account for the deviations in terms of cohesive forces between the molecules similar to those he had postulated in deducing his pressure volume isotherms for gases. Van Laar (Z. physik. Chem., 72, 723, 1910; 83, 599, 1913) extended this point of view and obtained an equation which may be written as

$$RT \log a_2 = RT \log N_2 + aN_1^2$$

where a_2 = activity of component "2"

a = a function of Van der Waals' "a" constant,

N_1 and N_2 = molar fractions of the respective components.

More recently Hildebrand (J. Amer. C. S., 39, 1452, 1916) has referred the deviations to differences of internal pressures of the two liquids. If the internal pressures of the two liquids are the same then in a solution each molecule may be under the same

forces as in its pure liquid. The vapour pressure is determined merely by the proportion of the two kinds of molecules present. But, if the internal pressures are different, deviations from Raoult's law may occur. Recently, Hildebrand (J. Amer. C. S., 51, 66, 1929) has shown that the equation,

$$RT \log a_2/N_2 = b N_1^2,$$

or its equivalent,

$$\log a_2/N_2 = \frac{1}{RT} (b. N_1^2 + c. N_1^3 + \quad),$$

which is used when the parabolic curve of molar heat of mixing against molar fraction proves unsymmetrical, applies to a large class of binary mixtures, which he termed regular solutions. This equation is similar to that of Van Laar's quoted above. The terms have the same significance, b and c, to a first approximation, are not functions of temperature. Hildebrand and Wood (J. Chem. Physics, Volume I, 817, 1933) have also given a modified equation,

$$\overline{F}_0 - F_2^0 = RT \log N_2 + A_{12} v_1,$$

where $A_{12} = V_2 \left\{ \left(\frac{E_2}{V_2} \right)^{1/2} - \left(\frac{E_1}{V_1} \right)^{1/2} \right\}^2$

where v_1 = volume of the fraction of the component 1,

E_1 and E_2 = cohesive energies,

V_1 and V_2 = volume of pure components.

If the molecular volumes are equal the above and this, Hildebrand's, equation become identical. The constants b and A_{12} in these equations are a measure of how far

these equations depart from ideal behaviour. Similar equations had been derived by Scatchard (Chem. Reviews, 8, 321, 1931) by making a somewhat arbitrary assumption about the energy of mixing. Bell (Chem. Soc. Annual Reports, page 26, 1933), in discussing the theory of solubility and related phenomena, points out that although the above and this Hildebrand's equations are applicable to non-polar liquids, there is no derivation that holds good for polar liquids. For this purpose it is therefore necessary to know the structure of the liquids.

Various attempts have been made to relate solubilities of non-polar substances to the (short-range) forces of interaction between the molecules. Harkins, Brown and Davies (J. Amer. C. S., 39, 354,1917) drew attention to the relationships between the mutual solubility of liquids and their related phenomena and remarked that "true solubility is a molecular scale phenomenon and is dependent upon the shapes and sizes of molecules which must be fitted together to make up a solution." A mathematical formulation of this idea has been given by Langmuir (Coll. Sym. Mono., 3,48, 1925). He makes use of his conception of "principle of independent surface action", according to which the potential energy of a molecule in a liquid is composed additively of the interactions at the different parts of the interface between the molecule

and its surroundings. Assuming that the molecules in the liquid are neither oriented nor segregated, but are arranged in a purely random manner, he obtained an expression for the evaporation of the pure substances, and if the molecule has two surfaces, the energy required to transfer a molecule from the liquid to the vapour phase is

$$\lambda = S\,(a\gamma_a - ab\gamma_{ab} + b\gamma_b),$$

where λ = the total surface energy,

γ = the energy of the fraction surface,

a and b = surfaces of the molecule.

This principle he further extends to the binary solutions and obtains an equation for two substances, A and B

$$\log f_A = \beta^2 S_A \phi \text{ and } f_B = \alpha^2 S_B \phi,$$

where f_A and f_B = activity of coefficients of substances A and B

and S_A and S_B = surface area of molecules A and B,

and α and β = surface fraction in solution,

ϕ = the "mixture energy."

If the molecules A and B have two kinds of surfaces, A and C, B and D and the fractional areas of which are a and c, b and d respectively, then

$$\phi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd},$$

where γ_{ab} = interfacial energy for the surface between A and B,

γ_{ad}= interfacial energy for the surface between A and D,

γ_{bc}= interfacial energy for the surface between B and C,

γ_{cd}= interfacial energy for the surface between C and D,

and so on.

Langmuir's theory has been tested by Smyth and Engel (J. Amer. C. S., 51, 2646, 1929) by determining the partial vapour pressures of a number of binary mixtures. They found that while there was qualitative agreement in the case of non-polar solutions, there were considerable discrepancies in other cases which they ascribed to the effect of dipoles. Butler, Thomson and Maclennan (J. C. S., 674, 1933) used the theory to interpret their results for vapour pressures and solubilities of normal aliphatic alcohols in water which show a general qualitative agreement with its requirements.

Expressions for the energy of interaction of a dipolar solute with the medium have been given by Martin (Phil. Mag., 8, 550, 1929) and Bell (J. C. S., 1371, 1931). Their expressions are referred to in Chapter V. They have been tested by ~~Maxtinx~~ Martin and George (J. C. S., 1413, 1933), Martin and Collie (J. C. S., 2658, 1932), who measured vapour pressures

of various phenyl derivatives having different polar groups in benzene, and by Bell (J.C.S., 2905, 1932), who determined the heat of solution of water and certain other polar molecules in various non-polar liquids.

Thermodynamics of binary solutions.

If $\overline{F}$ is the partial molar free energy of a substance in a solution and F° the molar free energy of the pure liquid at the same temperature, and p and p° its partial pressures in these two states, we have

$$\overline{F} = F^\circ + RT \log p/p^\circ \qquad (4).$$

When Raoult's law is obeyed, $p/p^\circ = N$; when it is not obeyed, the ratio p/p° may be termed the activity (α), which on this defination is unity in the pure liquid. The deviation from Raoult's law is thus expressed by the activity coefficient $f = \alpha/N$ or $f = p/p^\circ N$. We therefore may write

$$\overline{F} = F^\circ + RT \log fN \qquad (5).$$

If the solution is a very dilute one of the solute in the given solvent, f reaches its limiting value for infinite dilution in the given solvent. For such a solution, writing activity coefficient as f°, we have

$$\overline{F} = F^\circ + RT \log f^\circ N \qquad (6).$$

Now for this very dilute solution, Henry's law necessarily holds and it can easily be shown (Butler's Fundamentals of Chemical Thermodynamics , Volume II,

page 86) that the partial free energy can be expressed by

$$\bar{F} = \bar{F}^{0} + RT \log N \qquad (7)$$

where $\bar{F}^{0}$ = standard free energy for dilute solutions. Comparing (6) and (7), we see that

$$\bar{F}^{0} - F^{0} = RT \log f^{0} \qquad (8),$$

i.e., the difference between the standard free energy for dilute solution and the free energy of the pure liquid is $RT \log f^{0}$.

Butler, Thomson and Maclennan (loc.cit.) evaluated this quantity $\bar{F}^{0} - F^{0}$, by determining the activity co-efficients f^{0}, for a number of normal aliphatic alcohols in water at 25°C. Their results are given in Table I.

TABLE I

Alcohol	f^{0}	$\bar{F}^{0} - F^{0}$
Methyl	1.5.	240
Ethyl	3.48	740
n.- Propyl	12.5	1500
n- Butyl	46.5	2280
n.- Amyl	219	3190
n- Hexyl	903	4030
n.- Heptyl	3,560	4850
n.- Octyl	12,300	5580

They showed that $\overline{F}^\circ - F^\circ$ increased by approximately equal increments and that each additional $-CH_2$ group, as we pass up the series of aliphatic alcohols, contributed about 800 calories. They were able to give an approximate explanation of this relation in terms of Langmuir's theory.

However, this quantity is not very suitable for theoretical treatment since it depends on the behaviour of the substance in two states, (1) the dilute solution, (2) the pure liquid. The latter enters into the activity coefficient f°, on account of the quantity p_0. Since p_0 decreases rapidly as we pass up the series of alcohols, this alone accounts for a large part of increase in RT log f°.

It is therefore more suitable to take the substance in the state of vapour rather than that of the liquid as the reference state. If F°_g is the molar free energy of substance in vapour at unit pressure (1 mm. Hg), its free energy at another pressure p is

$$\overline{F} = F^\circ_g + RT \log p \qquad (9).$$

If, therefore, p is the partial pressure of the vapour over a very dilute solution of molar fraction N, since the partial free energies of the two phases in equilibrium must be equal, by equation (7), we have

$$\overline{F} + RT \log N = F^\circ_g + RT \log p$$

$$\text{or} \quad \overline{F}^\circ - F^\circ_g = RT \log p/N \qquad (10).$$

That is, RT log p/N measures the difference between the standard free energy for the dilute solution and the standard free energy in the vapour. This quality depends only on the interaction of the solute molecule and the solvent and may be called the free energy of solvation (or, in water, of hydration). Thus p/N is effectively a measure of the distribution ratio of the solute between the vapour and the solution and is also proportional to the Constant of Henry's law.

It may be determined, (1) by direct measurement of the partial vapour pressure in a sufficiently dil-utesolution, (2) when the solute and solvent are only slightly miscible, the ratio p/N for dilute solution is given by p°/N_S, where p° is the vapour pressure of the pure solute and N_S is its molar fraction in the diluted solution. Or, since when p and N refer to a suitably dilute solution, $f^\circ=p/p_0N$ or $p/N=f^\circ p^\circ$.

The values of N_S were determined by Butler, Thomson and Maclennan (loc. cit.) for the four normal aliphatic alcohols, C_5 to C_8, by solubility method and in order to use these values, it was necessary to know the vapour pressures of these alcohols at 25°C.

The vapour pressures of lower alcohols being known, it was therefore decided to determine the vapour pressures of the higher alcohols over a range

of temperature for which the extrapolation at 25°C. could be made, and also to check the values recorded of n-Butyl and n-Amyl alcohols.

The vapour pressures of a number of isomeric alcohols have also been determined. Some of these are not employed in the calculations; but the recorded data on these substances are very scanty and having purified specimens of these substances, it appeared to be worth while to use the apparatus to measure their vapour pressures also.

Chapter II deals with the vapour pressure determinations. In Chapter III are recorded direct measurements of p/N for a number of isomeric alcohols, which are not sufficiently immiscible to be suitable for the solubility method. In Chapter IV, these methods are extended to aqueous solutions of substances, containing polar groups of other kinds, and in Chapter V is a discussion of the significance of the results obtained.

C H A P T E R II

The vapour pressures of some aliphatic alcohols.

The vapour pressures of some aliphatic alcohols.

Experimental.

Purification of Materials.

Little information could be obtained upon the subject of purifying the alcohols, although Verkade and Coops (Trav. Chim. des Pays Bas, 46, 905, 1927) describe the preparation of the normal alcohols for combustion purposes. It was decided to rely upon fractionations with an efficient rectifying column to purify the pure quality samples of the alcohols supplied by the B. D. H.

All the fractionations were carried out using a long modified evaporator still head with an effective length of about 30 cms: and filled with glass rings, was fused with the distilling flask. The thermometer was arranged to have all the mercury

immersed in the vapour. All the corks were protected with tin foil and in this way contamination from corks, etc., was reduced to a minimum. n-Butyl, n-Amyl alcohols and its isomers were distilled at atmospheric pressure, but the higher alcohols, because of their high boiling points were distilled at reduced pressure. All heating was carried out by means of an oil bath.

Each alcohol was kept over freshly burnt quick lime for 24 hours in a stoppered flask, the contents being shaken at frequent intervals. It was refluxed for two days and then fractionated, the fractions thus obtained had the boiling points which remained constant to 0.1 - 0.2°C., it being found necessary to protect the head of the column with cotton wool to prevent fluctuations due to draughts. The higher alcohols were distilled at reduced pressure with a smaller column. Previous fractionations had been carried out from Calcium using Hempel column in determining their solubilities by Butler, Thomson and Maclennan (loc.cit.).

The boiling points of all the alcohols corrected to 760 mm. pressure together with their densities, $D_4^{25^\circ}$, at 25°C., compared with water at 4°C., and refractive indices, $n_D^{20^\circ}$ at 20°C., using D line, are given below. The corrected boiling points were ob-

tained from observations in the vapour pressure apparatus, with a correction to 760 mm. from the slope of vapour pressure curve. The densities were determined with a Sprengel type of a pyknometer and the refractive indices with a Pulfrich refractometer.

TABLE II

Alcohol	B.P./ mm.	B.P./760 mm.	$D_{4°}^{25°}$	$n_D^{20°}$
iso-Propyl	82.01-82.03°/748.4	82.39	0.7812_6	1.3688_6
n-Butyl	117.16-117.26/742.4	117.71	0.8059_3	1.3998_2
iso-Butyl	107.87-107.91/767.1	107.89	0.7983_3	1.3960_3
sec-Butyl	99.58-99.70/755.3	99.95	0.8029_9	1.3984_6
tert-Butyl*	81.77-81.87/733.4	82.75	-	-
n-Amyl	137.1-137.2/747.4	137.75	0.8125_3	1.4111_3
iso-Amyl	131.15-131.35/761.2	131.35	0.8102_2	1.4096_4
sec-Amyl	120.26-120.29/775.3	119.89	0.8052_5	1.4178_7
tert-Amyl	101.98-102.2/768.3	101.9	0.8059_9	1.4058_0
n-Hexyl	64.4-64.5/9	155.7	0.8183_5	1.4182_7
n-Heptyl	76.7-76.8/9	175.6	0.8205_3	1.4252_7
n-Octyl	89.1-89.2/9	194.5	0.8232_2	1.4295_7

* M.P. 25.5°

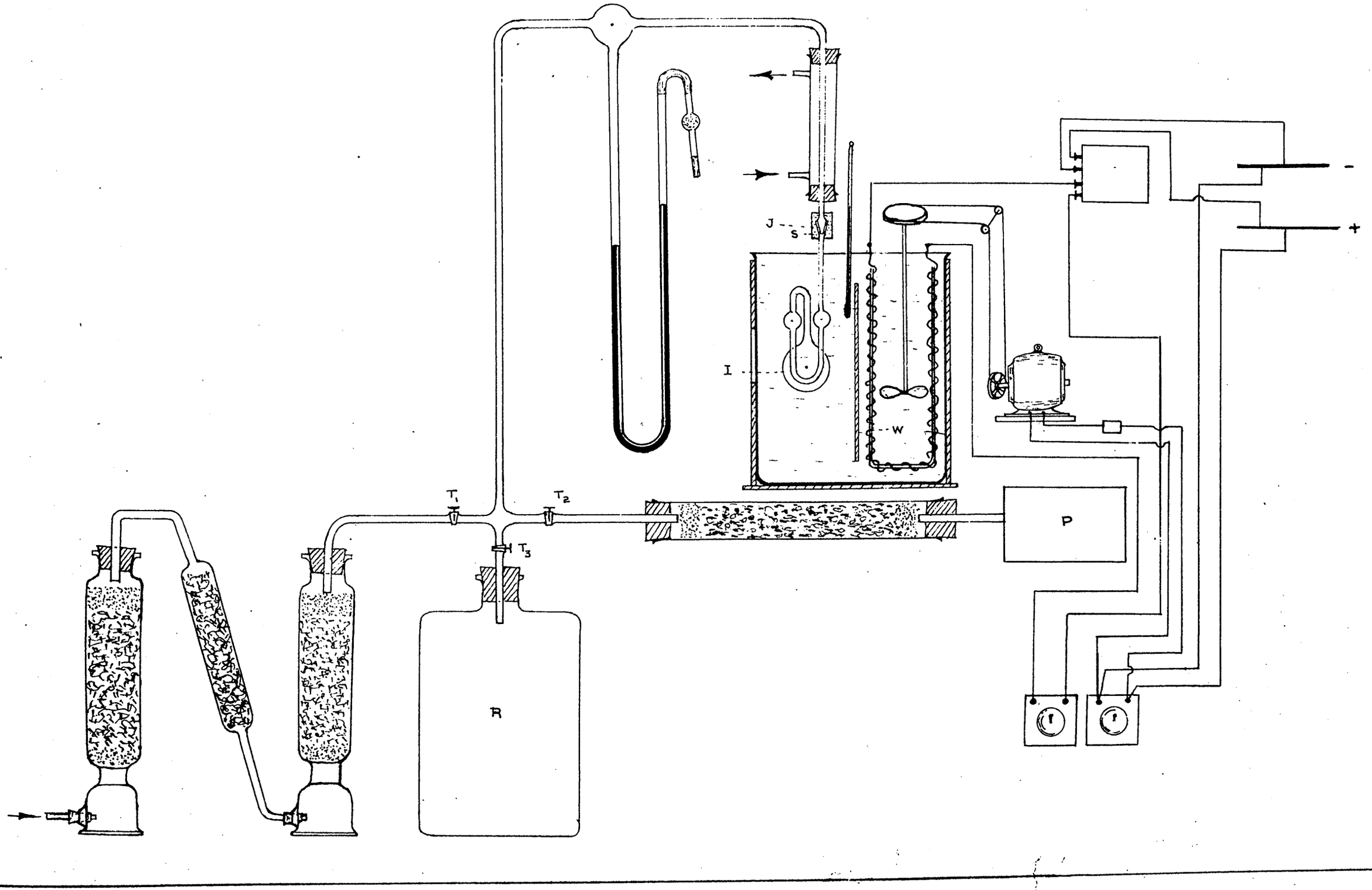
Apparatus.

The isotensiscope method was adopted for determining the vapour pressures at various temperatures. The apparatus followed the general outline of that described by Smith and Menzies (J.Amer.C.S., 32, 1412, 1910) and

is indicated diagrammatically in Figure 1. As far as possible the apparatus was made of one piece of glass. For filling the isotensiscope I had to be removeable and, for this purpose, was fitted on by means of a ground glass joint J, which was protected by a mercury seal S. To avoid contamination of the alcohol from the air in the apparatus, the air entering was passed through towers of $CaCl_2$ and Soda-Lime. The lead to the pump P was also protected with a P_2O_5 tube. The air reservoir R was protected from draughts by asbestos. Immediately above the isotensiscope was a cold water condenser. The isotensiscope was immersed up to the ground glass joint in a bath of glycerol, held in a large beaker, lagged with several layers of asbestos sheeting, and fitted with an asbestos lid with apertures for the apparatus. A window was cut in the asbestos at the side to allow of observation of the levels in the U-tube of the isotensiscope.

The glycerol was heated by passing current, obtained from the A. C. mains through a transformer, through a coil of platinum wire W, wound on a glass rod and immersed in the bath. Efficient stirring was obtained from a fastly revolving paddle, the glycerol being partly divided into two compartments by copper gauze to make a good continuous current of liquid from stirring. The working thermometers, which had very wide scales, were calibrated in a similar bath of

Figure 1



glycerol held in a very tall beaker which could immerse the standard thermometers completely. The working thermometers were immersed only as far as they would be in actual use. The stirring again was exceptionally brisk and simultaneous readings were taken on two thermometers while the temperature fell very slowly during cooling.

During the experiment the temperature was maintained at any agreed temperature by manipulating the switch in series with the heater, while the mercury level in the thermometer was watched through a telescope, this giving good magnification and completely avoiding parallax errors. After a little practice with this method, it was found easy to maintain the temperature constant to within $\pm 0.01°$ at temperatures below 100° and to within 0.02° at temperatures above 100°. The main error in the temperature would therefore appear to be in the behaviour and calibration of the thermometers. The standard thermometers were newly obtained from N.P.L. The Hg in the manometer was purified by distillation. Readings of the Hg levels were taken on a Casella Cathetometer which could be read by means of a vernier to 0.05 mm; and were always reproducible to within 0.1 mm. The barometer was the new Casella improved type, Fortin's Patent Standard Barometer. In both cases the Hg level

were corrected for difference of density of Hg to 0°C. Correction for g was not considered necessary.

Procedure.

Two persons were required to perform these experiments, one to keep the temperature steady by watching it through a telescope and the other to adjust the levels in the U-tube of the isotensiscope, to take the reading on the cathetometer and to note the barometer and room temperature.

The liquid under investigation was put in the isotensiscope by means of a clean pipette and transferred into its extreme bulb, whose capacity was 10 cc., along with a piece of porous tile, which served to maintain continuous equilibrium between the liquid and the vapour phase and at the same time to expel any dissolved air present in the liquid. The isotensiscope was then fixed in position and the mercury seal fixed. Tap I (Figure 1), which served as an ingress for the air, was then closed. Taps II and III were then kept open and the apparatus and the reservoir evacuated which took about 15 minutes. Meanwhile the temperature of the glycerol bath was adjusted to any specified temperature at which the first observation was to be

made. The liquid began to vaporise from the bulb, condensed in the condenser, which returned to form the liquid seal in the U-tube.

When this had been formed the air inlet (Tap I) was slightly opened and the pressure carefully adjusted by levelling the liquid in the U-tube, which indicated the equality of pressure in the two limbs. As the adjustment was rather sensitive, it was necessary at times either to evacuate further or to pass more air. When the levels had thus been carefully adjusted, the readings of the levels of mercury in the two limbs of the manometer were taken with the cathetometer. At the same time room temperature and barometer was noted. In this way evacuating and resetting again for several times, several readings at the same temperature, in the beginning were taken until consistent values for the vapour pressure were obtained. This consistency indicated that this treatment had rendered the liquid free from air.

The temperature of the bath was then raised to some other specified temperature and at the same time air was being let in very gradually, just sufficient to maintain the levels in the U-tube, until equilibrium had been established at the new temperature. Proceeding in this way, vapour pressures of the liquid were determined.

Three sets of readings, with the fresh sample of the same alcohol, were taken at the same temper-

atures as before, and those were found to agree very closely with one another. In the final results the mean readings were taken. The curve, obtained in each case by plotting the logarithms of vapour pressure against the reciprocal of absolute temperature, was found to be nearly a straight line with a very slight curvature. The vapour pressures of higher alcohols from C_5 to C_8 were taken from 60° and upwards, and those of isomers of Butyl and Amyl alcohols were obtained from 25° and upwards excepting tert.-Butyl alcohol, being solid (m.p. 25.5°), for which measurements began at 30°C.

RESULTS:

In Tables IIa and IIb are given the results of vapour pressure values (p mm. Hg) of alcohols over a range of temperature (t°c). Their graphs of logarithm of vapour pressure (log p) against the reciprocal of absolute temperature (I/T) are indicated in Figure 2. Of these, agreement with previously recorded data is shown in four cases, viz., n-Butyl alcohol, Kalbaum (Z. physik. Chem., 26, 577, 1898); iso-Butyl and iso-Amyl alcohols, Schmidt (ibid, 8, 628, 1891); Richardson (J.C.S., 761, 1886) and tert-Butyl alcohol, Parks and Burton (J. Amer. C.S., 24, 50, 1928). The results for n-Amyl alcohol are not in agreement with those recorded by Grassi (Cim., 23, 109, 1888), while in remaining six cases no pressures over a range

of temperature have been recorded. The graph of recorded vapour pressure values of n-Amyl alcohol and those obtained in the present determination are indicated in Figure 3. The extrapolated values of vapour pressures of higher alcohols and tert-Butyl alcohol are given in brackets in Tables IIa and IIb.

TABLE IIa.

t°C	n-Butyl	iso-Butyl	sec-Butyl	tert-Butyl	sec-Amyl	tert-Amyl
25.03	6.78	11.56	17.15	(42.41)*	6.03	16.72
30.05	9.57	16.47	24.54	58.15	8.79	23.30
35.08	13.50	22.39	33.30	78.18	12.44	32.00
50.13	34.45	55.62	80.74	177.8	32.40	77.14
60.17	60.69	95.84	138.4	291.4	57.92	129.8
70.35	103.0	159.7	224.1	462.4	99.12	211.4
80.64	168.5	256.4	355.2	705.9	161.8	332.8
90.89	266.6	397.8	543.1	-	255.5	505.5
101.22	408.3	600.7	-	-	390.4	-
110.25	578.6	-	-	-	550.2	-

Figure 2

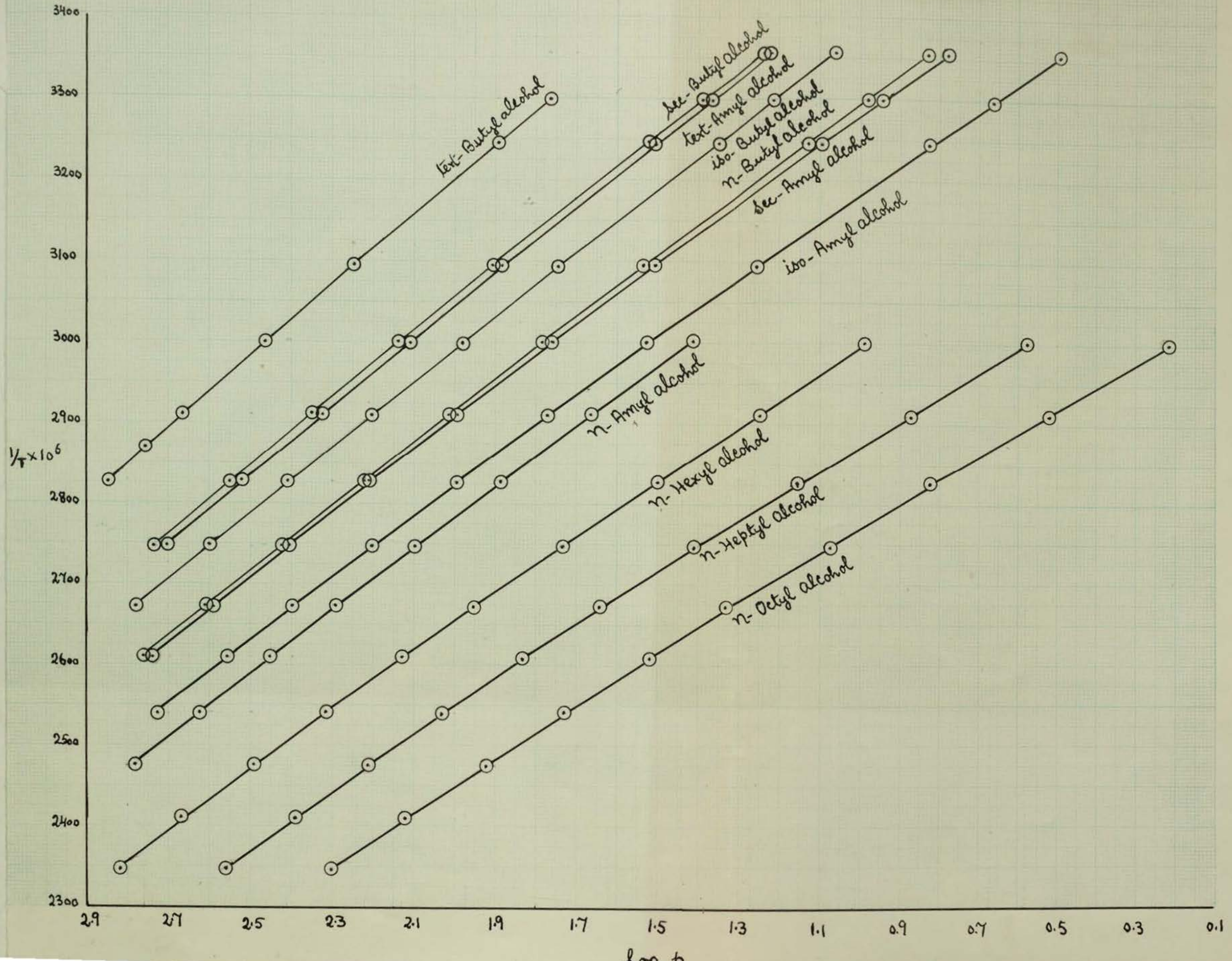
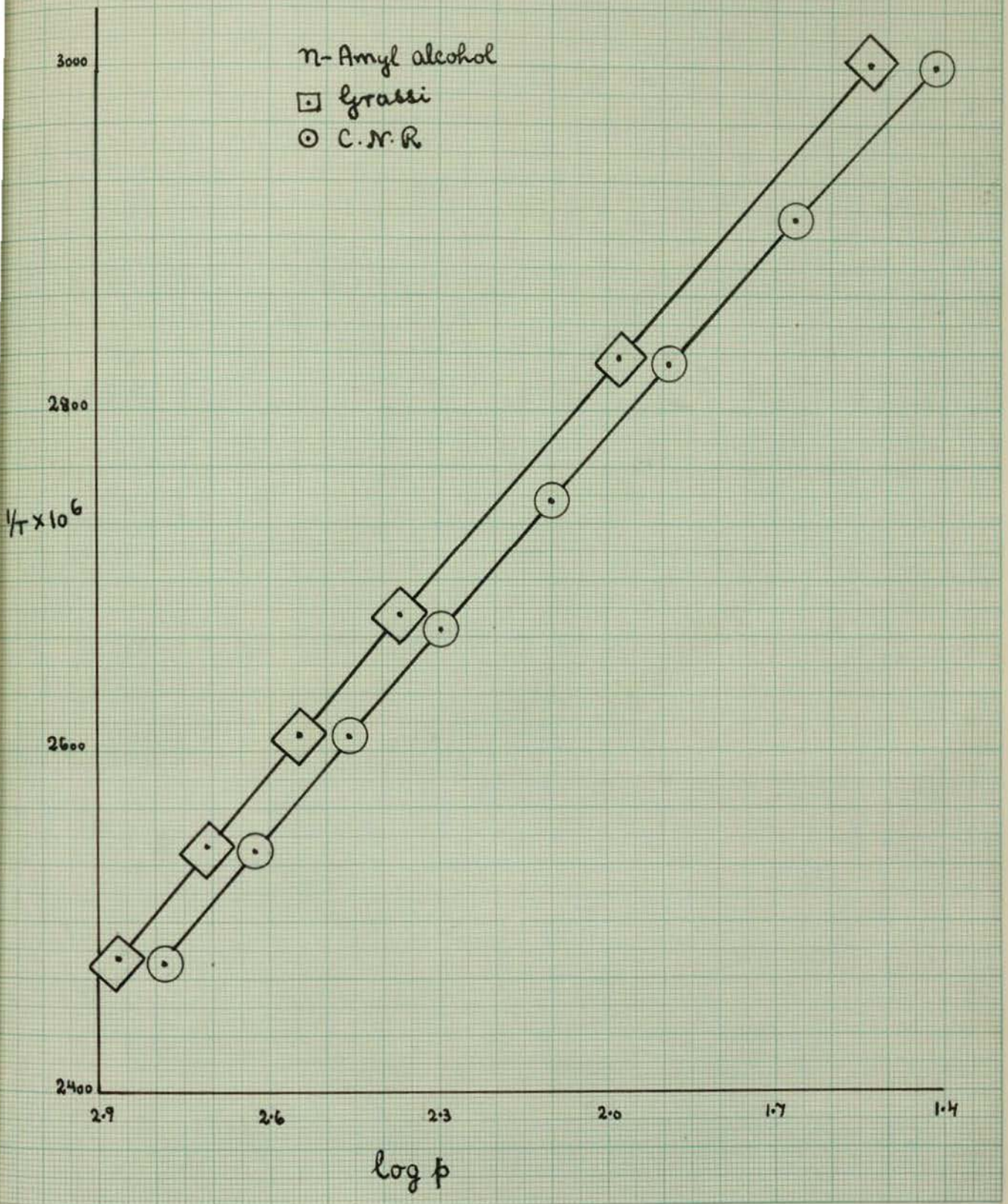

3400
3300
3200
3100
3000
2900
2800
2700
2600
2500
2400
2300
1/T x 10^6
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.3
0.1
log p
tert-Butyl alcohol
sec-Butyl alcohol
tert-Amyl alcohol
iso-Butyl alcohol
n-Butyl alcohol
sec-Amyl alcohol
iso-Amyl alcohol
n-Amyl alcohol
n-Hexyl alcohol
n-Heptyl alcohol
n-Octyl alcohol

TABLE IIb.

t°C	iso-Amyl	n-Amyl	n-Hexyl	n-Heptyl	n-Octyl
25.03	3.11	(2.50)	(0.719)	(0.224)	(0.0083)
30.05	4.61	-	-	-	-
35.08	6.75	-	-	-	-
50.13	18.09	-	-	-	-
60.17	33.78	26.01	9.75	3.79	1.65
70.35	59.27	46.15	17.74	7.48	3.31
80.64	99.52	77.74	31.60	14.35	6.68
90.89	160.6	125.8	54.57	25.73	11.92
101.22	251.5	198.0	90.01	44.12	21.51
110.25	361.2	286.9	135.1	67.96	33.42
120.61	532.3	424.1	207.2	107.2	54.02
130.94	-	611.9	309.8	163.6	85.43
141.73	-	-	456.8	246.5	132.6
152.83	-	-	659.8	364.5	201.5

Figure 3


n-Amyl alcohol
Eyrassi
C.N.R.
3000
2800
2600
2400
1/T x 10^6
2.9
2.6
2.3
2.0
1.7
1.4
log p

Interpolation formulae.

If ΔH is the latent heat of vaporisation, according to the Vant Hoff isochore, we have

$$\frac{d \log p}{dt} = \frac{\Delta H}{RT^2} \qquad (11)$$

where p = the vapour pressure of the substances,

T = the absolute temperature.

Writing $\Delta H = \Delta H_0 + \alpha T$, and integrating, we have

$$\log_{10} p = A - \frac{\Delta H_0}{2.303RT} + \frac{\alpha}{R} \log_{10} T$$

or $$\log_{10} p = A - \frac{B}{T} - C \log_{10} T \qquad (12)$$

where $B = \frac{\Delta H_0}{2.303R}$,

$C = -\alpha/R$,

A = integration constant.

This expression is suitable for expressing the vapour pressure over a fairly wide range of temperature.

The constants were found by determining H for each interval of temperature by

$$\log p_1/p_2 = -\frac{\Delta H}{R}\left(\frac{I}{T_1} - \frac{I}{T_2}\right) \qquad (13);$$

these values were plotted against the mean temperature to which they refer. The graphs of H against T, so obtained, were approximately linear and their slope gives α; from this the values of H_0 can now be obtained. The constants B and C are obtained in this way. A is evaluated by determining

$$\log_{10}p + \frac{B}{T} + C \log_{10}T \qquad (14),$$

for the whole series of measured values. If the interpolation formula fits the values exactly, A should be a constant. Actually in most cases the deviations from the mean value were small. Tables IIIa and IIIb show examples of the calculation of A. These two examples are shown as exhibiting the greatest and least agreement with the interpolation formula.

TABLE IIIa.

n-Butylalcohol.

(For vapour pressure values, p_1 and temperature, t°, see **Table IIa.**)

$$\log p = A - \frac{B}{T} - C \log T.$$

B = 4105)
) See Table IV
C = 10.35)

log p	$\frac{I}{T}$	$\frac{B}{T}$	10.35logT	A
0.8312	0.0033542	13.7690	25.6101	40.2103
1.1303	0.0032449	13.3203	25.7591	40.2097
1.5372	0.0030938	12.7001	25.9734	40.2107
1.7832	0.0030006	12.3175	26.1104	40.2111
2.0128	0.0029116	11.9521	26.2462	40.2111
2.2265	0.0028269	11.6044	26.3789	40.2098
2.4258	0.0027473	11.2777	26.5073	40.2108
2.6110	0.0026715	10.9665	26.6331	40.2106
2.7624	0.0026086	10.7083	26.7402	40.2109

Average A = 40.2105

TABLE IIIb.

n-Octyl alcohol

(For vapour pressure values, p, and temperatures, t°, see Table IIb.)

$$\log p = A - \frac{B}{T} - C \log T$$

B = 6190 } See Table IV.
C = 18.4 }

log p	$\frac{I}{T}$	$\frac{B}{T}$	18.4 log T	A
0.2175	0.0030006	18.5237	46.4185	65.2097
0.5198	0.0029116	18.0228	46.6599	65.2025
0.8248	0.0028269	17.4985	46.8958	65.2191
1.0763	0.0027473	17.0058	47.1240	65.2061
1.3326	0.0026715	16.5366	47.3477	65.2169
1.5240	0.0026086	16.1472	47.5381	65.2093
1.7326	0.0025399	15.7220	47.7512	65.2058
1.9317	0.0024750	15.3203	47.9582	65.2102
2.1225	0.0024106	14.9216	48.1688	65.2129
2.3043	0.0023478	14.5329	48.3798	65.2170

Average A = 65.2106

Table IV gives the values of the constants for all the alcohols. $\Delta\%$ is the average deviation (positive or negative) between the observed and calculated values. It can be seen that the accuracy is greater for the lower than for the higher alcohols. H_{298} is the latent heat of vaporisation at 25°C calculated for the values of H_0 and which are employed. The vapour pressures of the higher alcohols at 25°C were determined by means of these formulae, which are given in Table IIa.

TABLE IV.

Constants of the interpolation formulae.

Alcohol	A	B	C	$\Delta\%$	H_{298}
n-Butyl	40.2105	4100	10.35	0.12	12630
iso-Butyl	43.5513	4185	11.50	0.3	12340
sec-Butyl	43.4800	4110	11.50	0.5	12000
tert-Butyl	43.2834	3935	11.50	0.12	11200
n-Amyl	46.4925	4580	12.42	0.2	13600
iso-Amyl	51.5074	5120	16.10	0.6	13900
sec-Amyl	48.4849	4550	13.11	0.6	13060
tert-Amyl	47.4492	4280	12.88	0.15	11960
n-Hexyl	51.0030	5068	13.80	0.4	15020
n-Heptyl	56.1972	5580	15.41	1.5	16410
n-Octyl	65.2106	6190	18.40	1.0	17430

CHAPTER III.

The partial vapour pressures of some alcohols in very dilute aqueous solutions at 25° and their free energies of hydration.

The partial vapour pressures of some alcohols in very dilute aqueous solutions at 25° and their free energies of hydration.

The value of p/N can only be determined from the vapour pressure p_o and solubility N, when the alcohol is very slightly miscible with water. In order to find whether the p/N values were influenced by any constitutive factor, it was decided to make measurements with a number of isomeric propyl, butyl and amyl alcohols. These are moderately soluble in water, and in order to obtain this information direct determinations of the partial vapour pressures in very dilute aqueous solutions were made. The solutions were so dilute that it can be taken that the p/N ratios do not appreciably differ from the limiting values of infinite dilution.

Method of experiment.

The air bubbling method was adopted for determining the partial vapour pressures of these alcohols at known concentrations. This method has been extensively used by Perman (Proc. Roy. Soc. A., 72, 72, 1903); (Trans. Faraday Soc., 23, 95, 1927) for aqueous solutions, and by Foote and Scholes (J. Amer. C. S., 33, 1317, 1911), Dobson (J. C. S., 127, 2871, 1925), Shaw and Butler (Proc. Roy. Soc. A., 129, 519, 1930) and Butler, Thomson and Maclennan (loc. cit.) for determining the partial vapour pressures of the components of aqueous mixtures of the lower aliphatic alcohols.

This method depends upon the fact that, if air is bubbled through a solution under conditions such that equilibrium is attained, then the quantity of each volatile component in the vapour is proportional to its partial vapour pressure, and if the vapour obeys the ideal gas laws, according to Dalton's law of partial pressures, the partial vapour pressures of water and alcohol in the vapour are

$$\frac{p_a}{p_w} = \frac{W_a/M_a}{W_w/M_w}$$

where p_a = partial vapour pressure of alcohol,

p_w = partial vapour pressure of water,

W_a = weight of alcohol removed as vapour,

M_a = molecular weight of alcohol,

W_w = weight of water removed as vapour,

M_w = molecular weight of water.

In the very dilute solutions employed it can be assumed that Raoult's law applies to the solvent, i.e.,

$$p_w = p_w^\circ N_w,$$

where

p_w° = vapour pressure of water,

N_w = molar fraction of water,

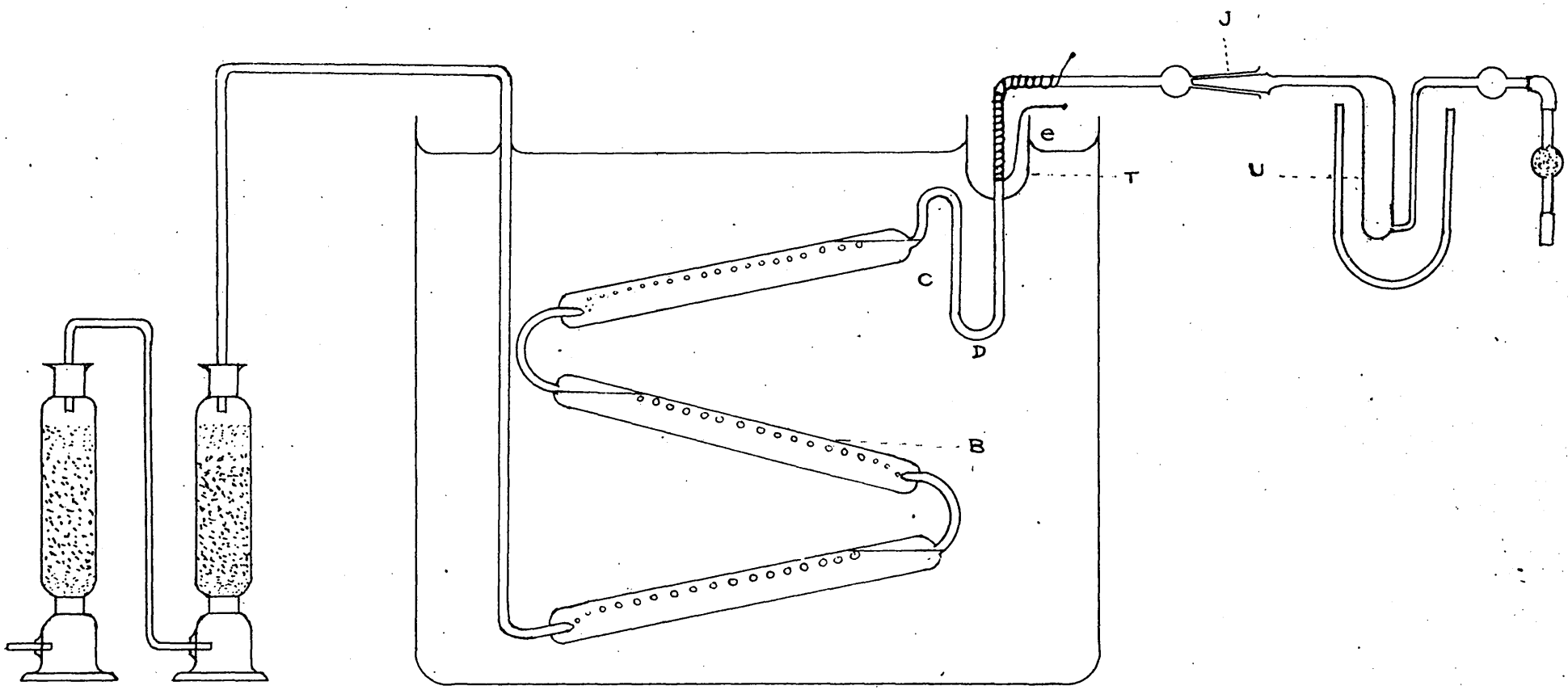
but N_w differs so little from unity (the lowest value is N = 0.999) that no practical error is made in these cases in assuming that $p_w = p_w^\circ$. The value of p_w° is taken as 23.77 mm. of Hg at 25°C (I.C.T.).

The relative proportions of alcohol and water in the small quantity of condensate was estimated by analysis in the Zeiss Industrial Interferometer, which was calibrated with solutions containing known proportions of alcohol and water. In some cases the condensate was diluted by a known amount so that every unknown solution lay within a certain range of composition over which the instrument was calibrated.

Apparatus and procedure.

The air bubbling apparatus (Figure 4) consisted mainly of two parts, (1) a bubbler for saturating the air with the vapours of a liquid under investigation

Figure 4



and water from the solution and (2) a collecting tube in which the vapours were condensed and their relative proportions determined.

The bubbler B consisted of three tubes fused together at a small angle of inclination to each other, and each containing a jet to produce a stream of small bubbles of air through any solution contained therein. Owing to the tubes being nearly horizontal the bubbles passed very slowly through each solution and so complete saturation was ensured. This was evident from the fact that reproducible results were obtained in each case, even with greatly different rates of flow of air through a solution. This was also confirmed by using a bubbler having four tubes instead of three, and it was found that the results in both the cases were in agreement with each other. Any droplets of liquid entrained in the air were precipitated by passing the vapours round a sharp bend in the exit tube of the bubbler as at cde. In order to prevent condensation of the vapours in the exit tube after the latter leaves the water in the thermostat, it was heated electrically by elements wound round the tubes from a point below the water level e. This was made possible by sealing a wide tube T on to the exit tube below the water level and winding the heating elements down into it. The tube T also

served to prevent a cold stream of air, caused by convection, impinging upon the bubbler just at the water level e. Prior to fitting tube T, this stream of cold air was the cause of some condensation at the point e. The horizontal portion of the exit tube was heated by means of an electric heating mat laid upon it and bent round it. The end of the exit tube was fitted with a standard ground glass joint J. The volume of bubbler was about 170 cc., so that small quantities of the liquid removed by evaporation did not appreciably alter the composition of the solution.

The standard ground glass joint J served to connect the bubbler to a collecting tube U immersed in a mixture of carbon dioxide snow and ether contained in a Dewar flask. This mixture was in the form of a sludge, and, therefore, in good thermal contact with the collecting tube. This fact coupled with the low temperature of the mixture, about -80°C, ensured complete condensation provided the rate of bubbling did not exceed a certain limit as found experimentally by Shaw and Butler (loc. cit.).

The bubbler was immersed in a thermostat, with glass sides, electrically heated and controlled to a temperature of 25°C $\pm$ 0.01°C.

The air was passed through Calcium Chloride and

Soda-lime towers before entering the bubbler. All the solutions were made up by weight from the pure materials and distilled water, kept in flasks with well fitting ground glass and rubber stoppers. Each solution was run into the bubbler as quickly as possible from a funnel.. The bubbler was then placed in position in the thermostat, the heating mats and elements switched on to the mains. After a few minutes to allow the tubes to heat, a stream of air was bubbled through the solution for about ten minutes, to saturate the solution with air and ensure that the conditions at the beginning of the experiment would be the same as those at the end.

Meanwhile the collecting tube, fitted with ground glass stoppers at both ends to prevent evaporation of the volatile condensate, was carefully cleaned, dried and suspended in the balance case for half an hour and then weighed. A small Calcium Chloride tube was then attached to its free end and the air in thetube displaced by dry air which was sucked in gently. It was then placed in position in the flask containing freezing mixture, which was covered with cotton wool to prevent the evaporation of the freezing mixture. The preliminary bubbling was now stopped and the tube connected to the bubbler by means of the ground glass joint J, and all the heating mats and elements switched on so that all

the exposed portions were well heated before beginning the experiment. The air was then allowed to pass at a suitable rate, and to give enough condensate it was found necessary to pass the air for at least 24 hours, and in some cases even for 48 hours. The condensate so obtained was allowed to attain the room temperature, and if it was in one phase was allowed to flow round the inside of the tube to ensure mixing with any liquid which had not run down into the bulb, was then compared in a Zeiss Industrial Interferometer with a suitable reference solution, which in most cases was distilled water. If it was in two phases, the tube was wiped carefully and allowed to stand in the balance case for thirty minutes, and weighed. Sufficient water was then added to it to form one phase, weighed again to determine the quantity of water added, and the resulting solution analysed in the Interferometer. The dial readings so obtained were found to be reproducible within a reasonable margin.

The Interferometer cells used were approximately 0.5 cm., 1 cm., and 5 cm., consisted of two compartments, L and R. The liquid of lower refractive index, i.e, the reference solution, was always put into the compartment R and the condensate to be examined into the compartment L. After a little practice with this

instrument it was quite possible to recognise the right set of fringes.

Solutions of known composition were then placed in the compartment L with reference solutions in R, and the dial readings obtained at which the two sets of fringes coincided. As far as possible the standard solutions were made up to give the dial readings which were in the near vicinity of the condensate readings. By plotting on a large scale the dial readings against the composition of the calibration solutions, the composition of the condensate was determined. The error of the Interferometer reading itself is small, and it is often possible to determine the solute concentration to within 0.001 per cent (by weight). The different condensates obtained from the same solution, however, differed by considerably more than this.

At least two reasonably concordant values were obtained for each solution.

RESULTS.

DETERMINATION OF THE COMPOSITION OF THE CONDENSATES:

Following are the detailed experimental results obtained in determining the composition of condensates.

N= molar fraction of the alcohol in solution,

x= weight per cent of alcohol in the condensate.

Alcohols marked with an asterisk formed one phase in the condensate, while the others formed two phases. In the latter case,

w = weight of the condensate,

s = weight of the condensate + water added,

p = weight per cent of the alcohol in diluted solution. (s).

* n-Propyl alcohol.

i = interferometer reading for 1 cm. cell with condensate in L and water in R.

$N \times 10^{3}$	i	average i	x
	1686		
0.929	1685	1689	3.66
	1696		

The following table gives the calibration values for 1 cm. cell of the interferometer with the solutions of alcohol in L and water in R.

wt. per cent. n-Propyl OH	Dial Reading
3.627	1675
3.663	1692

The graph of these results is indicated in Figure 5.

x

iso-Propyl alcohol.

i = interferometer reading for 1 cm. cell (reversed), with condensate in L and 9.805 weight per cent. solution in R.

$N \times 10^3$	i	average i	x
	2228		
0.986		2258	4.49
	2289		

The following table gives the calibration values for 1 cm. cell of the interferometer (reversed), with the solutions of alcohol in L and 9.805 weight per cent. solution in R.

wt. per cent. iso-Prolyl OH	Dial Reading
4.300	2363
5.041	1947

The graph of these results is indicated in Figure 5.

n-Butyl alcohol.

i = interferometer reading per 5 cm. cell with solution in L and water in R.

$N \times 10^3$	w	s	i	p	x	Mean x
	0.3423	2.5884	1630	0.738	5.58	
0.992						5.81
	0.2144	1.8291	1576	0.708	6.04	

The following table gives the calibration values for 5 cm. cell of the interferometer with the solutions of alcohol in L and water in R.

wt. per cent. n-Butyl OH	Dial Reading
0.702	1565
0.750	1652

The graph of these results is indicated in Figure 5.

iso-Butyl alcohol.

i = interferometer reading for 5 cm. cell (reversed) with S in L and approximately 5 wt. per cent. solution in R.

N x 10^3	W	s	i	p	x	Mean x
	0.4199	0.7700	330	4.933	9.05	
1.143						9.00
	0.4402	0.8160	631	4.826	8.95	

The following table gives the calibration values for 5 cm. cell of the interferometer (reversed), with the solutions of alcohol in L and approximately 5 wt. per cent solution in R.

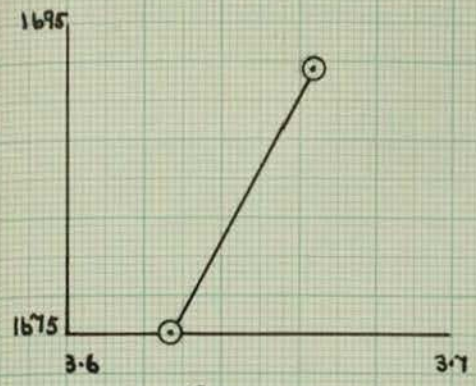
Wt. per cent. iso-Butyl OH	Dial Reading
4.889	453
4.997	152

The graph of these results is indicated in Figure 5.

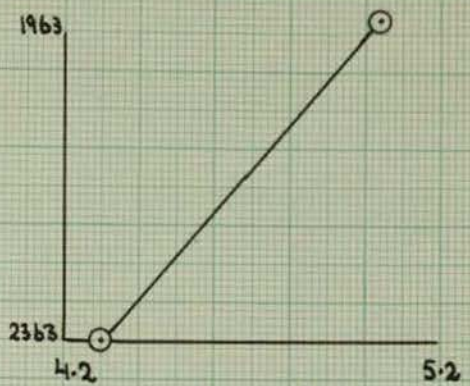
* sec-Butyl alcohol.

i = interferometer reading for 0.5 cm. cell with condensate in L and water in R.

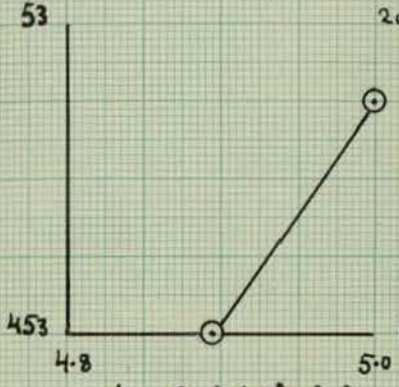
Figure 5



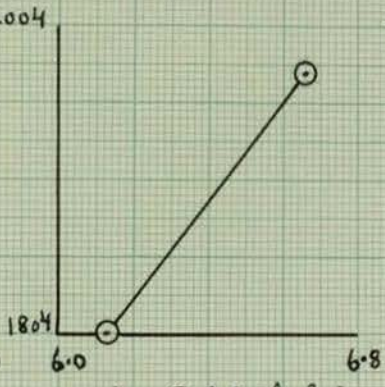
n-Propyl alcohol



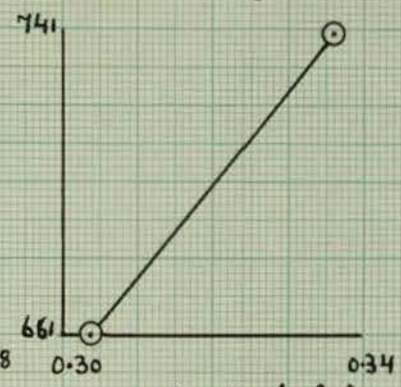
iso-Propyl alcohol



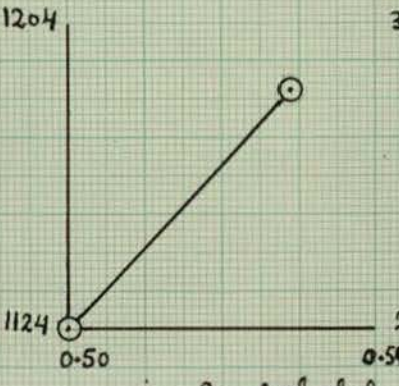
iso-Butyl alcohol



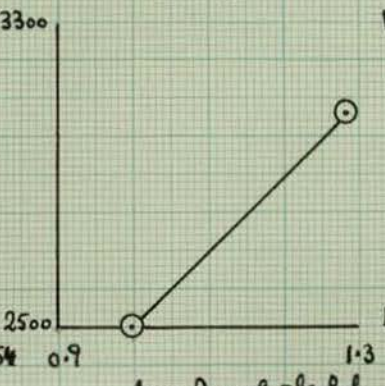
Sec-Butyl alcohol



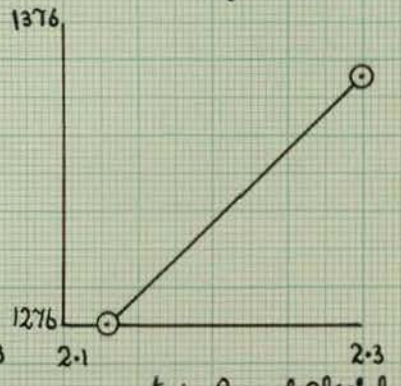
n-Amyl alcohol



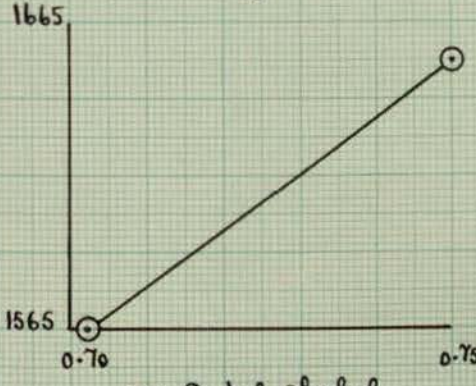
iso-Amyl alcohol



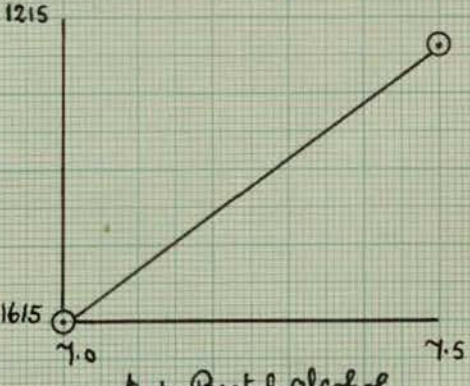
Sec-Amyl alcohol



tert-Amyl alcohol



n-Butyl alcohol



tert-Butyl alcohol

Vertical axes = Dial Reading
Horizontal axes = Wt o/o alcohol

$N \times 10^3$	i	average i	x
	1974		
0.959		1985	6.68
	1996		

The following table gives the calibration values for 0.5 cm. cell of the interferometer, with the solutions of alcohol in L and water in R.

wt. per cent. sec-Butyl OH	Dial Reading
6.126	1804
6.661	1974

The graph of these results is indicated in Figure 5.

* tert-Butyl alcohol.

i = interferometer reading for 1 cm. cell (reversed), with condensate in L and 9.137 wt. per cent. solution in R.

$N \times 10^3$	i	average i	x
	1274		
0.937		1272	7.55
	1270		

The following table gives the calibration values for 1 cm. cell of the interferometer (reversed), with the solutions of alcohol in L and 9.137 wt. per cent. solution in R

wt. per cent. tert-Butyl OH	Dial Reading
6.999	1615
7.500	1302

The graph of these results is indicated in Figure 5.

n-Amyl alcohol.

i = interferometer reading for 5 cm. cell with S in L and water in R.

$N \times 10^3$	w	s	i	p	x	Mean x
	0.6239	9.0354	725	0.334	4.75	
0.468						4.87
	0.2181	3.2589	674	0.311	5.00	

The following table gives the calibration values for 5 cm. cell of the interferometer with the solutions of alcohol in L and water in R.

wt. per cent. n-Amyl OH	Dial Readings
0.304	661
0.336	730

The graph of these results is indicated in Figure 5.

iso-Amyl alcohol.

i = interferometer reading for 5 cm. cell with S in L and water in R .

$N \times 10^3$	w	s	i	p	x	Mean x
	0.5428	6.0051	1200	0.535	5.92	
0.506						5.83
	0.5699	6.3454	1155	0.515	5.73	

The following table gives the calibration values for 5 cm. cell of the interferometer, with the solutions of alcohol in L and water in R.

wt. per cent. iso-Amyl	Dial Reading
0.501	1124
0.529	1186

The graph of these results is indicated in Figure 5.

sec-Amyl alcohol.

i = interferometer reading for 5 cm. cell with S in L and water in R.

$N \times 10^3$	w	s	i	p	x	Mean x
	0.6032	2.8147	3035	1.270	5.93	
0.496						5.98
	0.6721	3.1386	3085	1.292	6.03	

The following table gives the calibration values for 5 cm. cell of the interferometer with the solutions of alcohol in L and water in R.

wt. per cent. sec-Amyl OH	Dial Reading
0.997	2499
1.282	3058

The graph of these results is indicated in Figure 5.

tert-Amyl alcohol.

i = interferometer reading for 1 cm. cell with S in L and water in R.

$N \times 10^3$	w	s	i	p	x	Mean x
	0.5152	2.5870	1303	2.198	11.05	
1.033						11.03
	0.6563	3.2102	1343	2.259	11.01	

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of alcohols in L and water in R.

wt. per cent. tert-Amyl OH	Dial Reading
2.299	1370
2.156	1276

The graph of these results is indicated in Figure 5.

PARTIAL VAPOUR PRESSURES OF THE ALCOHOLS IN DILUTE AQUEOUS SOLUTIONS AT 25°C.

In Table VI are collected the experimental results of the partial vapour pressures of the alcohols. In this table

N = molar fraction of the alcohol in solution,

x = composition of the condensate (wt. per cent.),

p = partial vapour pressure in mm. Hg.

TABLE VI

Alcohol	$N \times 10^3$	x	p	p/N
n-Propyl	0.929	3.66	0.270	291
iso-Propyl	0.986	4.49	0.334	339
n-Butyl	0.992	5.81	0.356	359
iso-Butyl	1.143	9.00	0.571	499
sec-Butyl	0.959	6.68	0.413	431
tert-Butyl	0.937	7.55	0.471	503
n-Amyl	0.468	4.87	0.249	532
iso-Amyl	0.506	5.83	0.301	593
sec-Amyl	0.496	5.98	0.309	622
tert-Amyl	1.053	11.03	0.601	582

The final results of investigation are given in Table VII, where

p° = vapour pressure of alcohol,

N_s = solubility of alcohol expressed in molar fraction.

The vapour pressure values of methyl, ethyl and n-propyl alcohols at 25° are taken from I. C. T. and that of iso-propyl from Shereshefsky (J. Amer. C. S., 50, 2966, 1928). The distribution ratios p/N (Column 3) are those obtained by direct measurement of the partial pressure of very dilute solutions, except in the case of methyl and ethyl alcohols, which are obtained by extrapolation from the values at higher concentrations, and those marked with an asterisk, which are derived from the solubility. The values of $f^\circ = p/p_0N$ (Column 4) are calculated from Columns 1 and 3. The values for the lower alcohols are somewhat greater than the results of the previous investigations, which are given in Table I, because the present measurements of very dilute solutions show that in making the extrapolation of $p/p^\circ N$ from N = 0.01 to zero concentration, too great an allowance had previously been made for

the flattening of the curve in dilute solutions.

The accuracy of the vapour pressure determinations depends on the correctness of the condensate composition. The greatest variations of the latter observed in repeated experiments with the same or similar solutions amounted to about 10 per cent., but in most cases, particularly when dilution of the condensate was unnecessary, a much small variation was obtained. An uncertainty of 5 per cent. in the partial pressure corresponds to about ±30 calories in RT log p/N. Taking into account the numerous instrumental factors which enter into the determinations, an error of ±40 calories may be allowed in individual cases.

TABLE VII

Distribution ratios of aliphatic alcohols between the vapour and dilute aqueous solutions at 25°C, and related quantities.

Alcohol	p°	I/N_0	p/N	p/p_0N	$RT\log p/N$
Methyl	122.2	-	184	1.51	3090
Ethyl	59.0	-	218	3.69	3190
n-Propyl	20.1	-	291	14.4	3380
iso-Propyl	44.0	-	339	7.7	3450
n-Butyl	6.78	53.1	360*		
	-	-	359	52.9	3490
iso-Butyl	11.56	-	499	43.2	3680
sec-Butyl	17.15	-	431	25.1	3590
tert-Butyl	42.41	-	503	11.8	3690
n-Amyl	2.50	219	547*		
	-	-	532	214	3730
iso-Amyl	3.11	-	593	191	3784
sec-Amyl	6.03	-	622	103	3812
tert-Amyl	16.72	-	582	35	3773
n-Hexyl	0.719	903	649*	903*	3840*
n-Heptyl	0.224	3,560	798*	3,560*	3960*
n-Octyl	0.083	12,300	1020*	12,300*	4110*

C H A P T E R IV

The partial vapour pressures of compounds of various types in dilute aqueous solutions and their free energies of hydration.

The partial vapour pressures of compounds of various types in dilute aqueous solutions and their free energies of hydration.

Having determined the free energies of hydration of a number of normal and isomeric aliphatic alcohols, it was decided to make similar measurements with compounds having different polar groups. The compounds chosen for comparison with the alcohols were amines, nitriles and carboxy-acids of the normal aliphatic series from C_2 to C_4. A few measurements have also been made of similar aromatic compounds, and also of

some esters and polyhydric alcohols.

The solubilities and vapour pressures of some of these substances were known, and in most cases the miscibility with water was too great for the application of the solubility method. It was therefore decided to determine their p/N values in very dilute aqueous solutions at 25°C by the bubbling method described in Chapter III. In the case of Benzonitrile, the solubility method was employed.

Materials.

The same precautions were taken in fractionating the following substances as mentioned in Chapter II. These materials were also supplied by the B.D.H.

Methyl-acetate.

The method adopted by Young (Proc.Roy.Soc., Dublin, 12, 344, 1910) was used. The ester was kept over anhydrous potassium carbonate for 12 hours to remove all the acid present in it. It was then treated with anhydrous phosphorus pentoxide which freed it from the traces of water and alcohol and then fractionated; the middle fraction having the b.p. 56.54°-56.64° at 745.5 mm. (corr. 57.15° at 760 mm.).

Ethyl-acetate.

This was also treated in the same way as Methyl-acetate and the middle fraction had the boiling point 77.10°-77.14° at 759.7 mm. (corr. 77.15° at 760 mm.).

Ethylene Glycol.

This was purified by the method given in Gatterman's "Laboratory Methods of Organic Chemistry", page 102. The Glycol was shaken with dry ether three or four times, and the contents poured into a separating funnel and allowed to settle. Glycol being heavier than ether formed the lower layer which was separated and heated to about 150°C to get rid of all the ether present in it. While hot it was poured into a distilling flask and fractionated, using a 12 bulb column. The heating was carried out by means of a metal bath. The middle fraction, distilling within 0.2°, was collected and had the boiling point 197.4° -197.6° at 763.7 mm. (corr. 197.3 at 760 mm.).

Glycerol.

In this case the A.R. product was used, which, according to the specification, contained 99.97 per cent. Glycerol and was free from any objectionable

impurity. It was therefore found unnecessary to distil this substance on account of its very hygroscopic nature. Its density and refractive index was found to be

$$D_4^{25^\circ}\ 1.2552_1\ ;\ n_D^{20^\circ}\ 1.4703_5.$$

n-Propionitrile.

This was purified by the method given by Thorpe (J.C.S., 37, 205, 1880). It was shaken three or four times with dilute hydrochloric acid in a separating funnel and heated with lime, which neutralised the remaining acid and also acted as a drying agent. It was then fractionated and the middle fraction had the boiling point 96.52°-96.62° at 747.4 mm. (corr. 97.2° at 760 mm.).

Benzonitrile.

This was purified by the method given in Sudborough and James' "Practical Organic Chemistry", page 202. The nitrile was treated with ether, in which it was soluble, and the ethereal solution washed with dilute sodium hydroxide and sulphuric acid solution and dried with calcium chloride. The ether was removed by heating it on a steam bath. It was

then fractionated, and the middle fraction had the boiling point 189.9°-190.3° at 760 mm.).

Ethylamine.

This was obtained in the form of Ethylamine hydrochloride. It was treated with sufficient strong sodium hydroxide solution to neutralise the acid and then heated. The Ethylamine liberated as gas was dissolved in distilled water. The strength of solution obtained was found to be 2.5 per cent (by weight).

Preparation of solutions.

All the solutions were roughly made by weight and their correct composition determined by liberation with hydrochloric acid of known strength.

The other substances were fractionated by distillation. The boiling points of their middle fractions along with their corrected boiling points at 760 mm. are given in Table VIII.

TABLE VIII.

Substance	B. P./mm.	B. P./760 mm.
n-Propylamine	49.01-49.31°/763.7	49.25°
n-Butylamine	77.01-77.32°/751.3	77.81
n-Propionic acid	140.25-140.35/743.6	141.25
n-Butyric acid	162.46-162.66/764.4	162.4
n-Butyronitrile	116.36-116.66/743.3	117.3
Phenol	181.3-181.6/762.1	181.2
Aniline	184.05-184.06/751.9	184.4

RESULTS.

DETERMINATION OF THE COMPOSITION OF THE CONDENSATES.

Following are the detailed experimental results obtained in determining the composition of condensate. As before,

N = molar fraction of the substance in solution,

x = wt. per cent. of the substance in condensate.

The substances marked with an asterisk formed one phase in the condensate while the others formed two phases. In the latter case,

w = weight of the condensate,

s = weight of the condensate + water added,

p = weight per cent. of substance in dilute solution.

Methyl-acetate.

i = interferometer reading for 1 cm. cell with s in L and water in R.

$N \times 10^3$	w	s	i	p	x	Mean x
	0.2944	1.3935	1783	5.252	24.86	
0.500						24.91
	0.4080	1.9146	1806	5.320	24.97	

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of ester in L and water in R.

wt. per cent. Methyl-acetate	Dial Reading
5.213	1770
5.302	1800

The graph of these results is indicated in Figure 6.

Ethyl-acetate.

i = interferometer reading for 1 cm. cell with s in L and water in R.

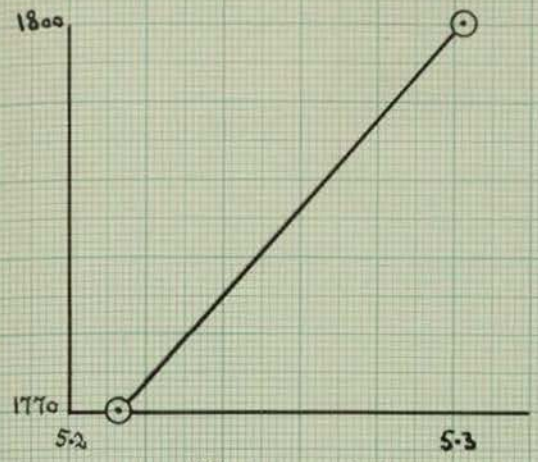
$N \times 10^3$	w	s	i	p	x	Mean x
	0.3657	5.4639	1482	3.513	52.49	
0.976						52.86
	0.4576	6.9808	1472	3.490	53.24	

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of ester in L and water in R.

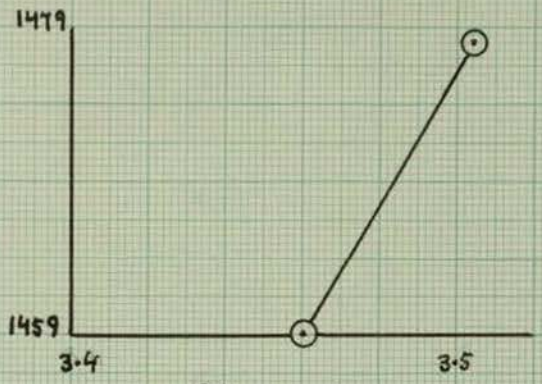
wt. per cent. Ethyl-acetate	Dial reading
3.460	1459
3.504	1478

The graph of these results is indicated in Figure 6.

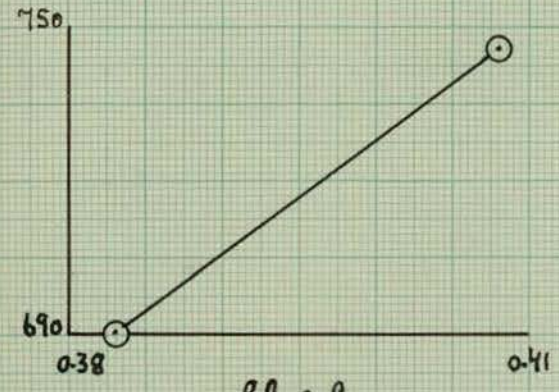
Figure 6



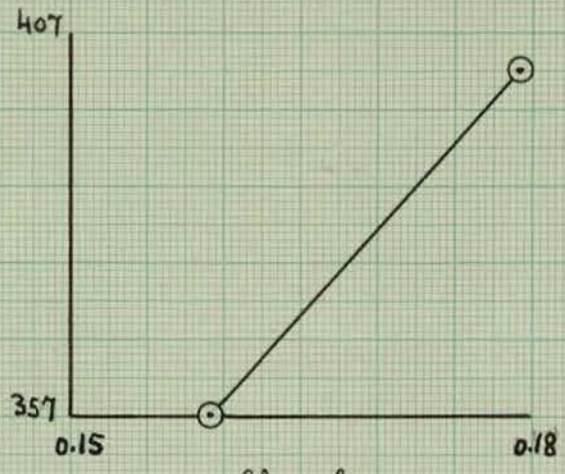
Methyl-acetate



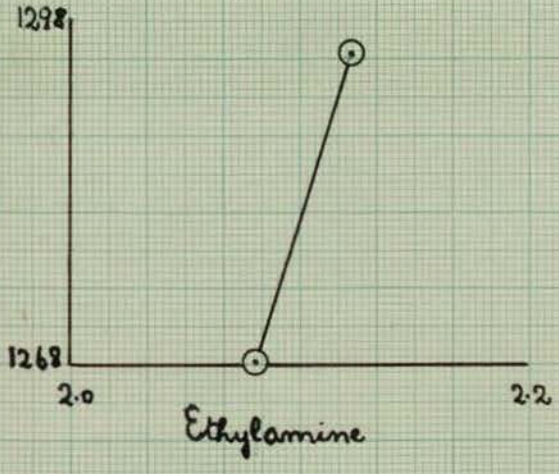
Ethyl-Acetate



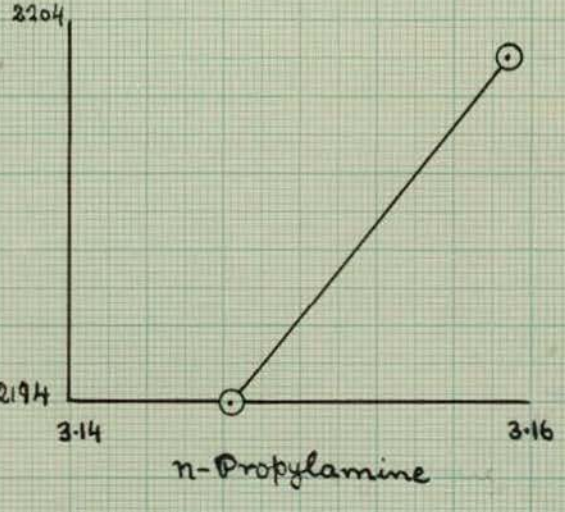
Glycol



Glycerol



Ethylamine



n-Propylamine

Vertical axes = Dial Reading
Horizontal axes = Wt of Substance

* Ethylene Glycol.

i = interferometer reading for 5 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	690		
10.37		702	0.39
	714		

The following table gives the calibration values for 5 cm. cell of the interferometer, with the solution of Glycol in L and water in R.

weight per cent. Glycol	Dial Reading
0.383	690
0.408	746

The graph of these results is indicated in Figure 6.

*Glycerol.

i = interferometer reading for 5 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	377		
10.93		382	0.17
	387		

The following table gives the calibration values for 5 cm. cell of the interferometer, with the solutions of Glycerol in L and water in R.

weight per cent. Glycerol	Dial Reading
0.159	357
0.179	402

The graph of these results is indicated in Figure 6.

Ethylamine

i = interferometer reading for 1 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	1282		
0.484		1283	2.10
	1284		

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of Ethylamine in L and water in R.

wt. per cent. Ethylamine	Dial Reading
2.080	1268
2.122	1295

The graph of these results is indicated in Figure 6.

n-Propylamine.

i = interferometer reading for 1 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	2185		
0.445		2197	3.15
	2210		

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of n-Propylamine in L and water in R.

wt. per cent. n-Propylamine	Dial Reading
3.147	2194
3.159	2203

The graph of these results is indicated in Figure 6.

n-Butylamine.

i = interferometer reading for 0.5 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	2340		
0.588	2353	2351	6.03
	2360		

The following table gives the calibration values for 0.5 cm. cell of the interferometer with the solutions of n-Butylamine in L and water in R.

Wt. per cent. n-Butylamine	Dial Reading
6.022	2340
6.037	2355

The graph of these results is indicated in Figure 7.

n-Propionic acid.

i = interferometer reading for 1 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	716		
5.021		729	1.59
	742		

The following table gives the calibration value for 1 cm. cell of the interferometer, with the solutions of n-Propionic acid in L and water in R.

wt. per cent. n-Propionic acid	Dial Reading
1.582	725
1.604	738

The graph of these results is indicated in Figure 7.

n-Butyric Acid.

i = interferometer reading for 1 cm. cell with condensate in L and water in R.

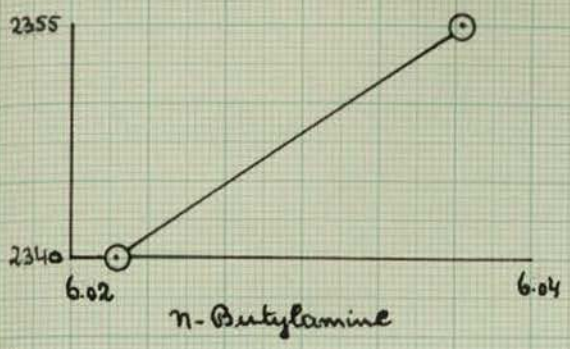
$N \times 10^3$	i	average i	x
	453		
2.089		452	0.96
	451		

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of n-Butyric acid in L and water in R.

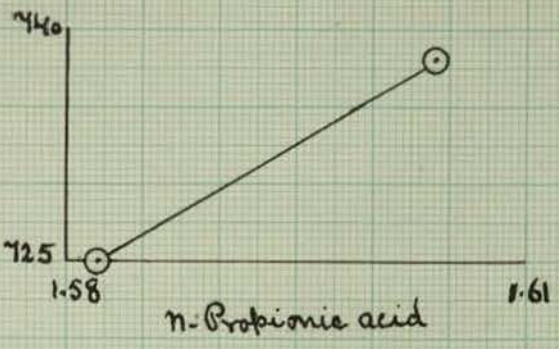
wt. per cent. n-Butyric acid	Dial Reading
0.958	451
1.002	476

The graph of these results is indicated in Figure 7.

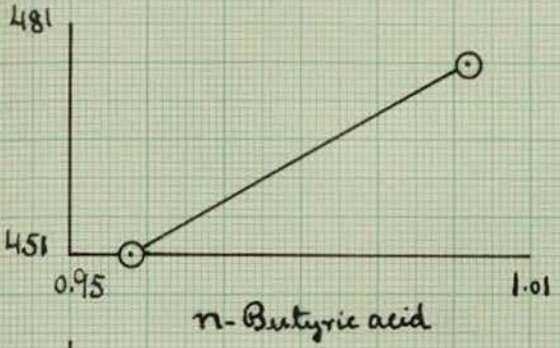
Figure 7



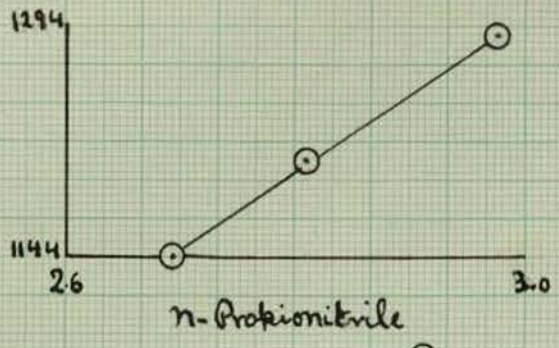
n-Butylamine



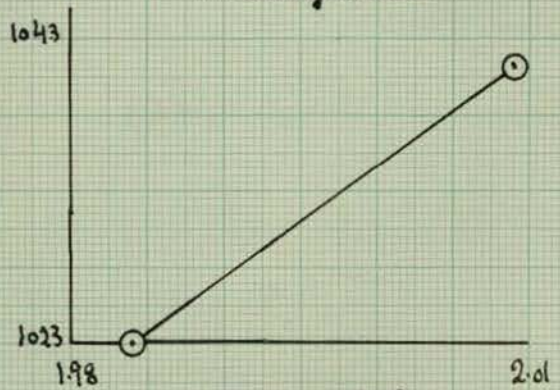
n-Propionic acid



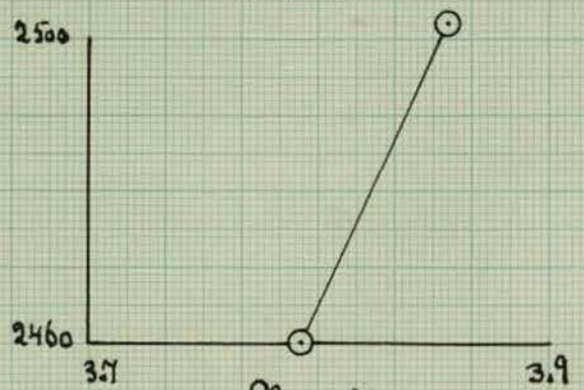
n-Butyric acid



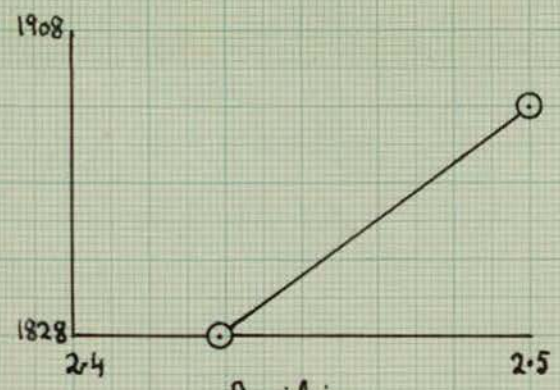
n-Propionitrile



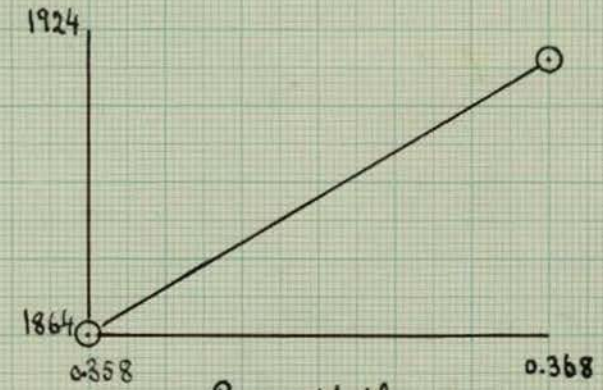
n-Butyronitrile



Phenol



Aniline



Benzonitrile

vertical axes = Dial Reading
Horizontal axes = wt o/o Substance

n-Propionitrile.

i = interferometer reading for 1 cm. cell with s in L and water in R.

N x 10^3	w	s	i	p	x	Mean x
	0.1778	1.1380	1240	2.889	18.49	
1.111						18.42
	0.3073	2.0277	1186	2.779	18.36	

The following table gives the calibration values for 1 cm. cell of the interferometer with the solutions of n-Propionitrile in L and water in R.

wt. per cent. n-Propionitrile	Dial Reading
2.693	1144
2.811	1202
2.975	1288

The graph of these results is indicated in Figure 7.

n-Butyronitrile.

i = interferometer reading for 1 cm. cell with s in L and water in R.

N x 10^3	w	s	i	p	x	Mean x
	0.3070	4.0040	1030	1.994	26.07	
0.984						25.82
	0.2712	3.4672	1035	2.001	25.56	

The following table gives the calibration values for 1 cm. cell of the interferometer, with the solutions of n-Butyronitrile in L and water in R.

wt. per cent. n-Butyronitrile	Dial Reading
1.984	1023
2.009	1041

The graph of these results is indicated in Figure 7.

* Phenol.

i = interferometer reading for 0.5 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	2491		
10.94		2502	3.86
	2513		

The following table gives the calibration values for 0.5 cm. cell of the interferometer, with the solutions of Phenol in L and water in R.

wt. per cent. Phenol	Dial Reading
3.792	2460
3.856	2502

The graph of these results is indicated in Figure 7.

* Aniline.

i = interferometer reading for 0.5 cm. cell with condensate in L and water in R.

$N \times 10^3$	i	average i	x
	1849		
1.334		1855	2.46
	1861		

The following table gives the calibration value for 0.5 cm. cell of the interferometer, with the solutions of Aniline in L and water in R.

wt. per cent. Aniline	Dial Reading
0.432	1828
2.500	1888

The graph of these results is indicated in Figure 7.

Solubility of Benzonitrile.

An analytical method was adopted for determining its solubility. About 5 cc. of the substance with 50 cc. of water were put in a U-tube, of the type previously used by Butler, Thomson and Maclennan (loc. cit.) for determining the solubilities of higher normal aliphatic alcohols. The U-tube was placed in a shaker and shaken for 24 hours in a thermostat at 25°C to ensure complete saturation. The contents were then allowed to settle. Benzonitrile being heavier than water formed the lower phase. About 10 cc. of the saturated solution were pipetted out in a flask which was stoppered and placed in the balance case for half an hour. It was then weighed and a quantity of water was added to it to reduce the concentration below the saturation point, and weighed again. The resulting solution was analysed in the interferometer. The results are tabulated below.

Benzonitrile.

w = weight of the solution from U-tube,

s = weight of the solution from U-tube + water added

i = interferometer reading for 5 cm. cell with s in L and water in R.

p = wt. per cent. of Benzonitrile in diluted solution (s).

x = wt. per cent. of Benzonitrite in w (solubility).

w	s	i	p	x	Mean x
10.9670	13.0946	1884	0.362	0.432	
10.8070	13.0672	1876	0.360	0.436	0.435
10.8523	12.9996	1897	0.364	0.436	

The following table gives the calibration values for 5 cm. cell of the interferometer with the solutions of Benzonitrile in L and water in R.

wt. per cent. Benzonitrile	Dial Reading
0.358	1864
0.368	1918

The graph of these results is indicated in Figure 7.

PARTIAL VAPOUR PRESSURES OF VARIOUS COMPOUNDS IN DILUTE SOLUTIONS AT 25°C.

In table IX are collected the experimental results the partial vapour pressures of the compounds. As before,

N = molar fraction of the substance in solution,

x = composition of the condensate (weight per cent.),

$p_.$ = partial vapour pressure in mm. Hg.

The p/N values of the substances marked with an asterisk were obtained, (1) Acetic acid, Fredenhagen and Liebster (Z. physik. Chem. A., 162, 449, 1932), and n-Propyl-acetate, from solubility and vapour pressure results from I. C. T. The vapour pressure value of Benzonitrite at 25°C. was obtained by extrapolation from the values given in I. C. T. These are bracketed in the table.

TABLE IX

Substance	N x 10^3	x	p	p/N	RT log p/N
Methyl-acetate	0.500	24.91	1.916	3832	4890
Ethyl-acetate	0.976	52.86	5.445	5580	5110
*n-Propyl-acetate	0.391	-	(32.7)	8385	5350
Glycol	10.37	0.39	.026	2.55	555
Glycerol	10.93	0.17	0.008	0.71	-202
Ethylamine	0.484	2.10	0.204	421	3580
n-Propylamine	0.445	3.15	0.236	530	3720
n-Butylamine	0.588	6.03	0.376	639	3830
*Acetic acid	0.323	-	0.004	12.6	1500
n-Propionic acid	5.021	1.59	0.0926	18.5	1730
n-Butyric Acid	2.089	0.96	0.047	22.5	1850
n-Propionitrile	1.111	18.42	1.754	1579	4360
n-Butyronitrile	0.984	25.82	2.154	2189	4560
Phenol	10.94	3.86	0.180	16.4	1660
Aniline	1.334	2.46	0.116	87	2650
Benzonitrile	0.763	-	(0.794)	1041	4210

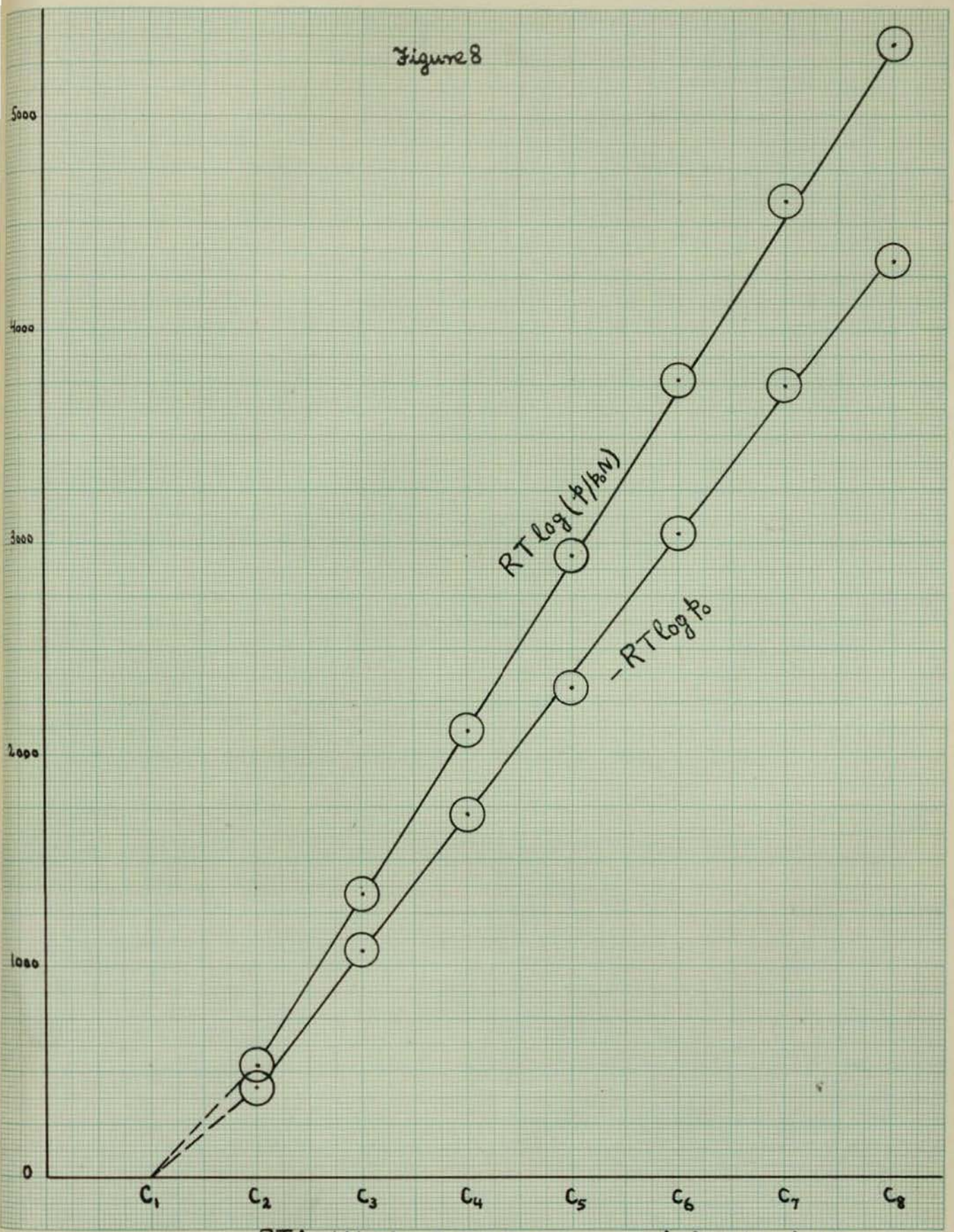
C H A P T E R V.

Discussion.

Discussion.

A. Aliphatic Alcohols.

Butler, Thomson and Maclennan (loc.cit.) found that in the series of normal aliphatic alcohols, the quantity RT log p/p_0N = RT log f^0 increases by an approximately constant increment. It is evident that since p_0 decreases as we pass from one normal aliphatic alcohol to the next in the series, that part of this increment arises from p_0. The first object of this investigation was to find how much of the total increment of p/p_0N was due to p_0. The values of the differences from methyl alcohol of RT log p/p_0N and of - RT log p_0 for the normal alcohols are plotted, in

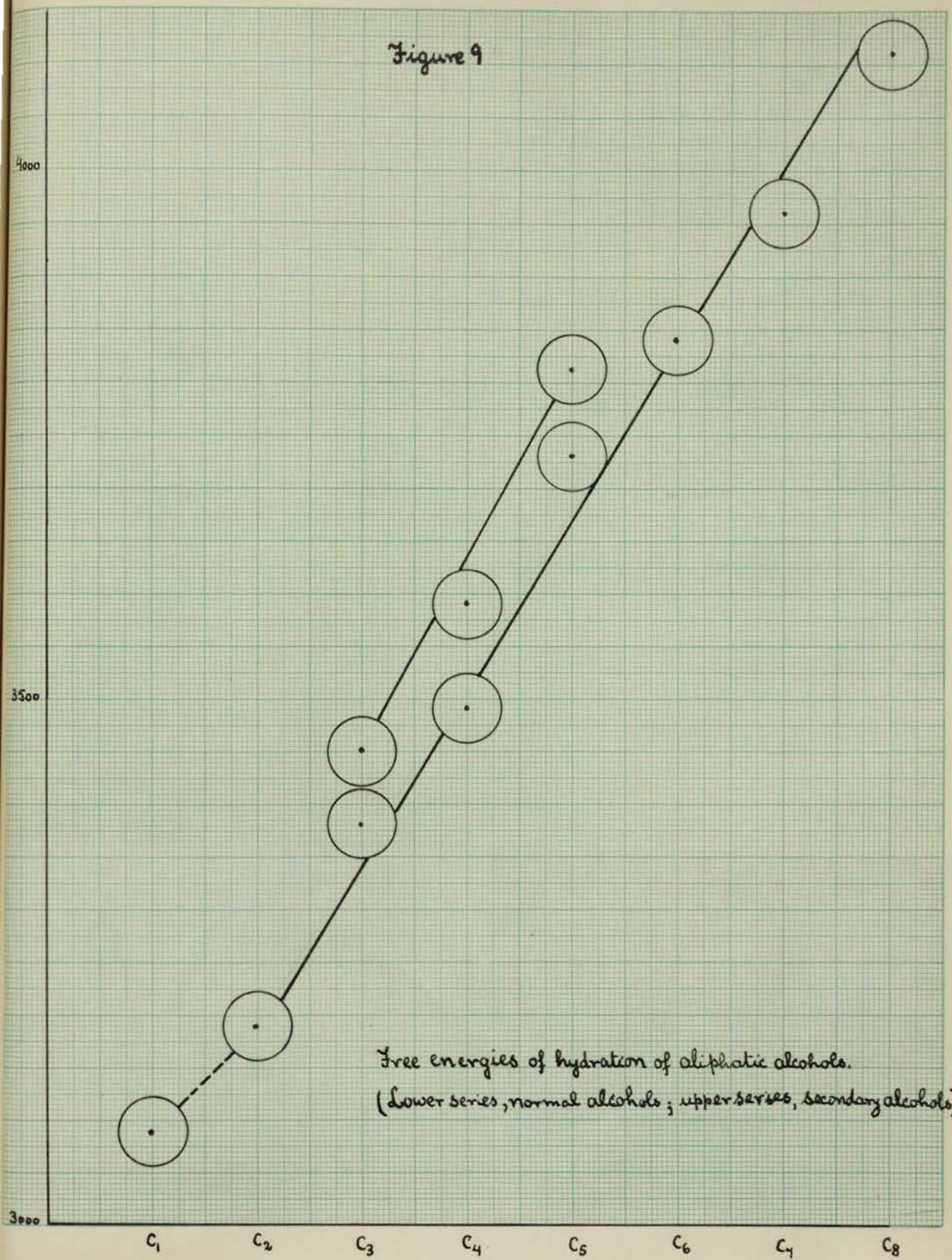


RT log (f/f₀ᴺ) and -RT log f₀ for normal aliphatic alcohols.

Figure 8, against the number of carbon atoms. It can be seen that while the average increment of RT log p/p_0N is about 800 calories for each $-CH_2$ group, the increment of - RT log p_0 is about 640 calories, leaving about 160 calories for the increment of RT log p/N. There is thus a real increase of RT log p/N or (p/N) as we pass up the series. The values of this quantity, which are derived from the measurements given in Chapter III, are shown on a large scale in Figure 9. The size of the radius of the circle indicates the experimental error. It can be seen that the whole series is compatible with a constant increment for $-CH_2$ group of 165 calories. The average increment from C_5 to C_8 is about 130 calories, while from C_2 to C_5 is about 180 calories. This difference may possibly be real and might be due to the completion of a ring in the five carbon chain, but the data is not sufficiently accurate to establish this.

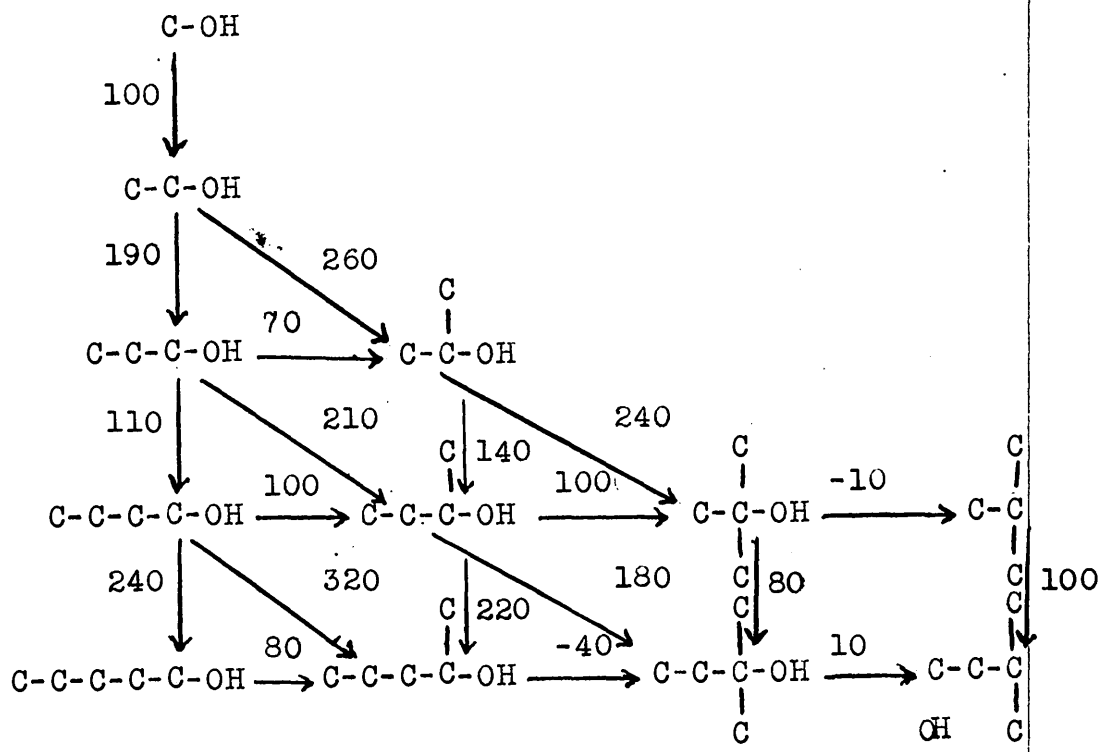
Turning now to the isomeric alcohols, the differences of p/N (Table VI) are not very great and in some cases not greater than the possible

Figure 9



Free energies of hydration of aliphatic alcohols.
(Lower series, normal alcohols; upper series, secondary alcohols).

experimental error. But some regularities can be made out as can be seen from the differences of RT log p/N values shown in the following scheme.

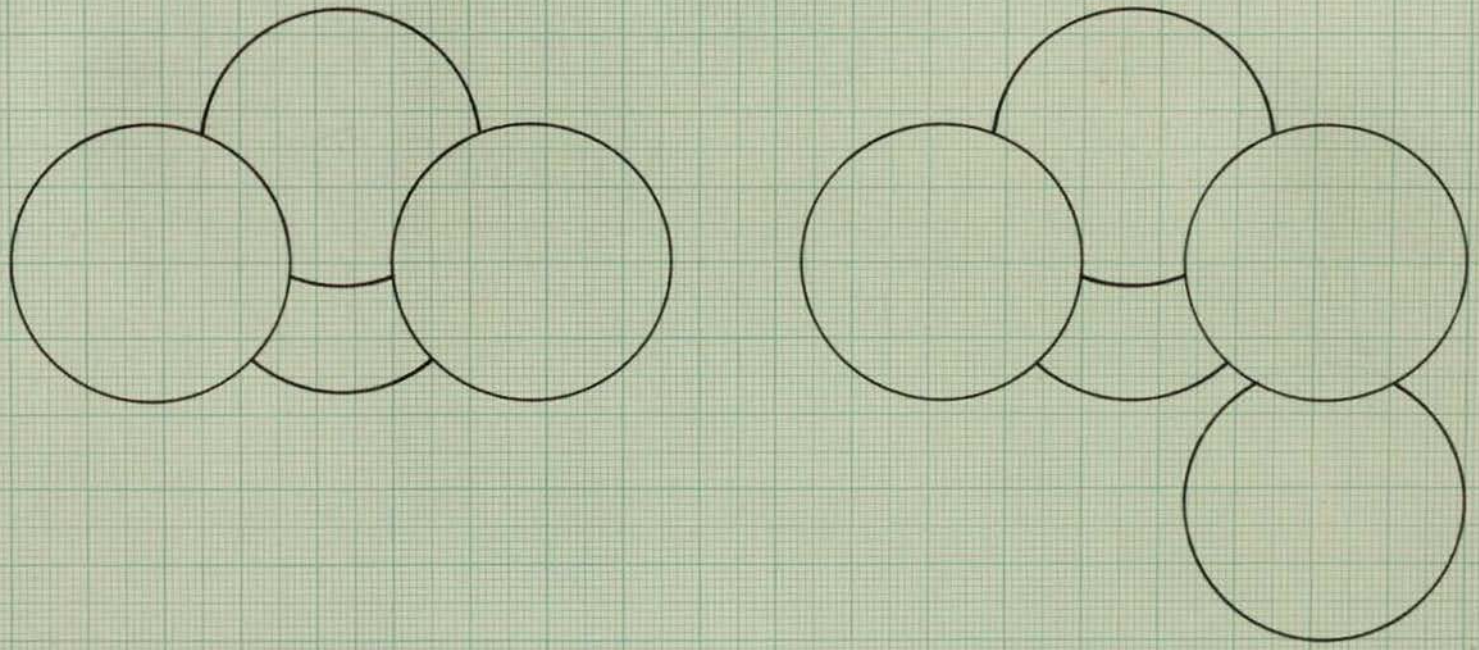


Thus the displacement of --OH group from a terminal carbon atom to next (giving a secondary alcohol) causes an increase in RT log p/N of about 100 calories. That is, while the addition of a $-CH_2$ group at the end of a straight chain gives an average increment of 165 calories, its addition to the α-carbon atom gives an increment of about 260 calories.

A further increment of the same order is observed when a second $-CH_2$ group is added in the α- position, giving a tertiary alcohol. A further constitutive influence also appears when the carbon chain is branched. The two butyl alcohols (iso and tertiary) having the nucleus (a), Figure 10, and the two amyl alcohols (iso and tertiary) with the nucleus (b) have nearly the same value of p/N, i.e., in both cases it appears to be immaterial to which carbon atom the -OH group is attached. This can be understood when the spatial arrangement of the carbon atoms is taken into account. The carbon atoms in the group (a) are arranged in a pyramid, and it can be seen that an -OH group attached to any one of the carbon atoms is similarly related to the other three. Similarly in group (b), the three carbons attached to one carbon atom form a pyramid, while the fourth has freedom of movement, but in aqueous solution its position of minimum energy is under the pyramid, forming a somewhat asymmetric hexahedron. An -OH group attached to either of these carbon atoms will now be somewhat similarly related to the others, irrespective of its position.

To sum up, the free energies of interaction of the normal aliphatic alcohols with water are clearly

Figure 10



(a)

(b)

additive within the experimental error. This quantity may be expressed by the formula

$$F \pm 50 \text{ calories} = 2850 + n(165),$$

where F = free energy of interaction,

n = number of $-CH_2$ groups,

and can be thus regarded as the sum of a quantity which is proportional to the number of $-CH_2$ groups.

The values for the isomeric alcohols are not readily expressible in an algebraic formula, and there appear to be two effects. (1) The energy of interaction of the -OH group with water may be reduced if it is shielded by the rest of the molecule to a greater extent, the free energy in solution being thereby increased. The increase of about 100 calories between the primary and secondary alcohols having the same straight chain appears to be an example. (2) A more compact arrangement of carbon atoms results in a smaller exposure of surface of the hydrocarbon residue to water and this gives rise to a decrease of F (i.e. an increase of solubility). This factor may however be balanced by a greater shielding of the -OH group in the more compact arrangement. Thus, while it is not at present possible to give precise explanation of these effects, the values obtained thus appear to

be compatible with a unitary theory of interaction between $-CH_2$ groups and water, when due regard is taken of the arrangement of groups in the molecule.

B. Compounds containing other polar groups.

The following compounds in Chapter IV were investigated in order to find the variation of RT log p/N, with the nature of polar group, in compounds having the same hydrocarbon radicals. The results are tabulated in Tables X and XIII.

TABLE X.

Radical	—OH	$-NH_2$	-COOH	—CN	-COO(R)
CH_3	3090	-	1500	-	-
C_2H_5	3190	3580	1730	4360	4890
C_3H_7	3380	3720	1850	4560	5110
C_4H_9	3490	3830	-	-	5350
C_6H_5	1661	2650	-	-	-

The following conclusions can be drawn from these data.

(1) In each series of aliphatic compounds the values RT log p/N increase as we pass up the series by approximately constant increments. The average value of the increment for each $-CH_2$ group is about the same as for the alcohols, but the range of divergence is somewhat greater. (2) The value of p/N is very considerably influenced by the nature of the polar end group, and in compounds containing the same number of carbon atoms in the hydrocarbon residue, the order is

$$-COO(R) > -CN > -NH_2 > -OH > -COOH,$$

and the solubilities of the vapours are thus in the reverse of this order. The order of the phenyl compounds so far as they have been investigated is the same, but the values are appreciably smaller than those of the corresponding ethyl compounds (i.e., the phenyl group confers a greater solubility on the compound than ethyl group.

It has been suggested that a significant part of the energy of interaction of a polar molecule with a solvent is the electrostatic energy of the dipole in the given medium. The energy of this interaction according to Bell (Trans. Faraday Soc., 27, 797, 1931; 30, 772, 1934), (J.C.S., 1371, 1931), who took as his model a spherical dipole with an electric doublet at

its centre, is

$$A = \frac{\mu^2}{3a^3} \cdot \frac{D-1}{2D+1}$$

where μ = dipole moment,

a = radius of sphere,

D = dielectric constant of medium.

Martin (Phil. Mag., 8, 550, 1929) made a similar calculation using as the model two oppositely charged spheres in contact and obtained the result

$$A = \frac{\mu^2}{3a^3}\left(1 - \frac{1}{D}\right).$$

On either of these calculations, the energies of interaction of different dipoles in a given solvent should be in the order of the values of $\mu^2/3a^3$ and for the purpose of making a comparison, we may assume that the free energies of interaction will be in the same order as the total energies. The hydrocarbon radical might be expected to have a shielding effect on the dipole, but in a series of compounds in which the radical is the same and the polar group different, this effect might be expected to be constant. The order of dipole moments of the polar groups in simple aliphatic and aromatic compounds is

$$-CN \rangle -OH \rangle -COO(R) \rangle -NH_2 \rangle -COOH.$$

This has no apparent relationship with the free

energies of hydration, but the use of proper values of a might modify this considerably. The following table, Table XI, is based on what may be regarded as reasonable estimate of the polar groups. It can be seen that the values of $\mu^2/3a^3$ still show no apparent relation with the solubilities.

TABLE XI.

	-CN	-OH	$-NH_2$	-COO(R)	-COOH
$\mu \times 10^{18}$	1.7	1.4	3.4	1.7	0.8
$a \times 10^{8}$	1.4	1.3	1.4	2.1	2.1
$\mu^2/3a^3 \times 10^{12}$	0.37	0.20	1.4	0.104	0.02
p/N (C_2 compounds)	1580	218	421	3847	18.5

The values, for dipole moments (μ) have been obtained from Sidgwick, Hampson and Marsden (Trans. Faraday Soc., 30, September issue Appendix, 1934) and of a for -CN, -COO(R), -COOH from Hassel's Kristall Chemie , $-NH_2$ from Bodtaker-Nœss and Hassel (Z. Anorgan. Chem., 211, 21, 1933) and of -OH from Bernal and Fowler (J.C.Phys., Vol. I, 515, 1933).

We conclude that the dipole interaction is not the determining factor at any rate in aqueous solutions. A comparison between acids and their isomeric esters and the alcohols and isomeric ethers, Table XII, shows that compounds containing the groups -COOH and -OH have a much greater solubility than isomeric compounds containing no hydroxyl group.

TABLE XII.

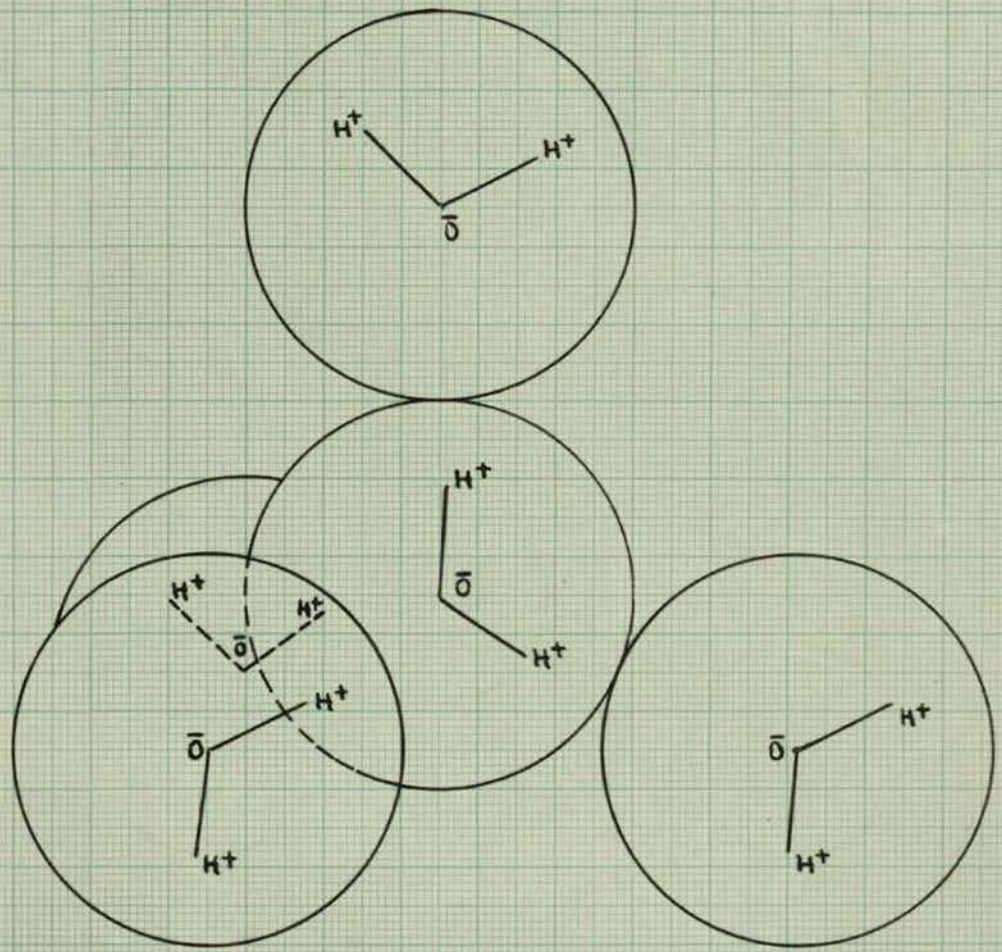
Substance	$\mu \times 10^{18}$	p/N	RT log p/N	Substance	$\mu \times 10^{18}$	p/N	RT log p/N
C_2H_5COOH	1.3	18.5	1730	CH_3COOCH_3	1.67	3850	3890
C_3H_7COOH	0.7	22.5	1850	$CH_3COOC_2H_5$	1.84	5580	5110
C_4H_9OH	1.65	360	3490	$C_2H_5OC_2H_5$ *	1.24	37200	6240
$C_5H_{11}OH$	-	540	3730	$C_2H_5OC_3H_7$ *	-	48200	6390
$C_6H_{13}OH$	1.64	650	3840	$C_3H_7OC_3H_7$ *	0.86	147000	7050

* Calculated from the solubilities in water and vapour pressures from I. C. T.

It is therefore probable that the determining factor in these compounds is the co-ordination of the hydroxyl group of the alcohol or acid with water. The model

suggested by Bernal and Fowler (loc. cit.) for mutual interaction of water molecules seems appropriate. According to this, the two hydrogens of the water molecules are arranged at approximately the tetrahedral with respect to the oxygen nucleus, and a water molecule can co-ordinate with four others as shown in Figure 11. Bernal and Fowler calculated the energy of interaction and obtained the value for the interaction of two water molecules, 5.7 kilocalories per molecule pair. If this conception be applied to the interaction of the alcohols, etc., with water, we see that the hydroxyl group of the alcohol molecule can co-ordinate in this way with three water molecules and the isomeric ether molecule with only two, for in the alcohol one of the tetrahedral positions is occupied by the hydrocarbon radical and on the ether two are so occupied. When an alcohol molecule is removed from the solution three hydroxyl-water bonds are broken and 3/2 water-water bonds take their place. If we suppose for a moment that the energy of the hydroxyl-water bond is the same as that of the water-water bond, we see that the energy of the removal of the alcohol molecule (so far as it is determined by the -OH group) is thus 3/2W, where W is

Figure 11



Tetrahedral co-ordination of water molecules. The four molecules surrounding one water molecule are shown. Of these, two are in the plane of the paper, one above and one below it.

the interaction energy for a single bond. Similarly when an ether molecule is removed from aqueous solution two bonds between $\rangle O$ and water are broken and one water-water bond takes their place, so that on the same assumptions, the energy change is W. Comparing then an isomeric ether and water molecule, the difference of energy on aqueous solution should be 3/2W-W=W/2. Bernal and Fowler's value of the every carbon-water bond is W=5.7 kilocalories per gram molecule, so that the difference of the energy of interaction of an alcohol and isomeric ether should be W/2=2850 calories per gram molecule. A similar difference should be found between the acid and the isomeric ester.

For a more precise calculation, it would be necessary to take into account the different distribution of electric charge in the R - OH or $\begin{matrix} R \\ \rangle O \\ R \end{matrix}$ groups, which is shown by the difference between their dipole moments and that of water. This is not possible at present, as the precise structures of these groups are unknown; but the qualitative agreement of the calculated with the observed value of these differences show that the calculation is on the right lines. It may be observed that the

calculation gives the total energy change, and it is necessary, for the purpose of making a comparison, to assume that the difference of the total and free energies is a constant in isomeric compounds.

Finally it is well known that the solubility of organic compounds in water is greatly increased by an increase of the number of -OH groups. Quantitative data on this effect are given by the determinations of p/N for ethylene glycol and glycerol. The free energies of hydration are given in Table XIII.

TABLE XIII.

Substance	RT log p/N	Substance	RT log p/N
C_2H_5OH	3190	C_3H_7OH	3380
$C_2H_4(OH)_2$	555	$C_3H_5(OH)_3$	-202

It can be seen that the change of RT log p/N between C_2H_5OH and $C_2H_4(OH)_2$ is -2630 calories, while that between C_3H_7OH and $C_3H_5(OH)_2$ is -3582 calories. The addition of -OH group therefore does not produce an additive effect. This indicates that when there are

two or more -OH groups in a molecule in close proximity with each other, the interaction of each with the surrounding molecule is influenced by the proximity of the others.

Summary.

1. Measurements have been made of (1) the vapour pressures of eleven aliphatic alcohols over a range of temperature, (2) the partial vapour pressures in very dilute aqueous solutions of ten aliphatic alcohols and fourteen compounds containing other polar groups, at 25°C.

2. From these measurements, together with the data previously published by Butler, Thomson and Maclennan (loc.cit.), values of free energy hydration ($\bar{F}^\circ - F^\circ_g = RT \log p/N$) at 25° of the normal alcohols from C_1 to C_8, of iso-propyl, three isomeric butyl, three isomeric amyl alcohols and fourteen compounds containing other polar groups have been obtained.

3. It is shown that in series of normal alcohols, of the increment of 800 calories for each additional $-CH_2$ found by Butler, Thomson and Maclennan (loc.cit.) in the quantity RT log p/N, (p/p_oN being the activity

coefficient of the alcohol in dilute aqueous solution referred to the pure liquid), about 640 calories is accounted for by the variation of RT log p_0, while the increment of RT log p/N is about 160 calories.

4. The isomeric alcohols show small, but apparently significant, differences, the nature of which is discussed.

5. In the compounds of other polar groups, $-NH_2$, -CN, -COOH and -COOR, show increments of the same order in the value of RT log p/N for additional $-CH_2$ group. The differences produced by these groups in compounds having hydrocarbon radical are considerable. They cannot be accounted for in terms of the simple electrostatic interaction of the group dipole with the medium, but it is shown by a comparison of the alcohols and isomeric ethers and of the acids and isomeric esters that the co-ordination of the -OH group with water is the most important factor. A calculation of the energy change of this co-ordination on the lines of Bernal and Fowler's calculation of the energy of co-ordination of two water molecules gives results of the right order of magnitude.

6. The free energies of hydration of ethylene glycol and glycerol have been determined. The con-

tribution of the -OH groups in these molecules to RT log p/N is not strictly additive.

In conclusion, I wish to express my thanks to Dr. J. A. V. Butler for his deep interest in the work, and for his many valuable suggestions; and to Dr. D. W. Thomson for his assistance in the vapour pressure measurements of Chapter III. I have also to acknowledge a grant, made to Dr. J. A. V. Butler, by the Committee of Moray Fund, which was used for the purchase of some of the substances used in this investigation.